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BY

Ira Remsen

*Professor of Chemistry in the Johns Hopkins University*

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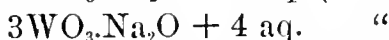
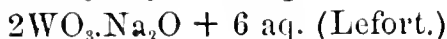
# AMERICAN CHEMICAL JOURNAL.

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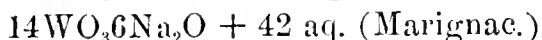
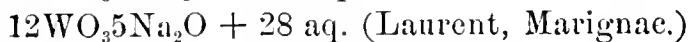
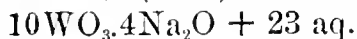
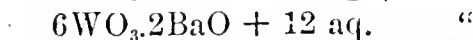
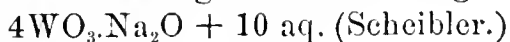
## ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.

In a letter addressed to Prof. Dana, printed in the *American Journal of Science and Arts*, and in another which appeared in the "Berichte" of the German Chemical Society, I have given a preliminary statement of my results in the study of the complex inorganic acids. The present notice is simply a report of further progress, and, like those which have already appeared, is to be regarded as provisional and subject to correction. I had proceeded but a little way in my investigations when I found it absolutely necessary to make a thorough study of the alkaline tungstates, which, as every chemist knows, are very numerous and varied in constitution. As the general result of my own study of the salts themselves and of the work of Scheibler, Marignac, Lotz, Forcher, Laurent, Lefort and other chemists who preceded me, I have arrived at a new classification and arrangement, which may be briefly stated as follows: There are two series of alkaline tungstates, the normal and the metatungstic series. To the normal series belong the salts respectively represented by the following formulas, which may be regarded as typical:



To the metatungstic series belong the following :



It will be seen that I have doubled several of the formulas which are usually received, and that in this way all the alkaline tungstates, the compositions of which have been well ascertained, are brought into simple and natural relations.

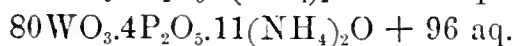
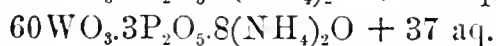
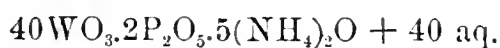
The antiquated mode of writing the formulas which I have employed presents the composition of the different salts in a clear point of view for the sake of comparison, and will therefore I hope be excused. I believe that it will be found that the alkaline molybdates admit of a similar classification, only the salts which we should naturally assign to the normal series are much more numerous, unless we consider some of those which belong apparently to this series to be acid. It may also be a question whether tungstates belonging to the type  $6\text{WO}_3.2\text{R}_2\text{O}$  exist, since, if we admit the existence of tri-salts like that of Lefort,  $3\text{WO}_3.\text{Na}_2\text{O} + 4 \text{ aq.}$ , we should have a case of isomerism. Besides the tungstates above referred to and assumed as types, I have repeatedly obtained a double salt of sodium, the analyses of which conform very closely to the formula,



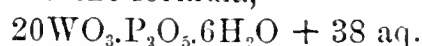
This may be written  $22\text{WO}_3.9\text{Na}_2\text{O} + 51 \text{ aq.}$  and the progress of science, which tends constantly to show that the structure of inorganic molecules is more complex than we formerly supposed, may possibly oblige us to again double the formulas of the alkaline tungstates and introduce the 22-atom salt as a special term.

My published results as regards the complex inorganic acids and their salts require correction in a few particulars. Thus I have no salt of phosphotungstic acid containing more than 6 atoms of base, the 7 and 8-atom salts proving to be either

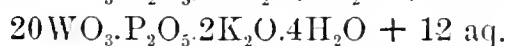
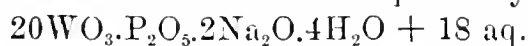
mixtures or salts of other series. The slightly soluble ammonium salts which I have obtained are represented by the formulas :



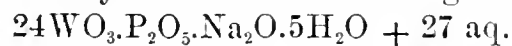
I regard all these as double salts, and have prepared barium salts corresponding to the two first mentioned. For the acid I find the formula,



considering it provisionally as six-basic. Two very well defined alkaline salts have respectively the formulas,

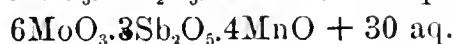
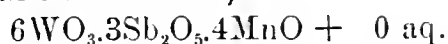


The ratio of 20 atoms of  $\text{WO}_3$  to 1 of  $\text{P}_2\text{O}_5$  is that which here represents the analyses, but I have some evidence of the existence of salts in which the ratio is 24 to 1 and 18 to 1. Thus the analyses of a sodium salt agree well with the formula,



Debray found the ratio of  $\text{MoO}_3$  to  $\text{P}_2\text{O}_5$  in one series of phospho-molybdates 20 to 1. Rammelsberg has much more recently found the ratio 22 to 1, and finally Finkener considers it to be 24 to 1. I am disposed to think that all three ratios exist among the phospho-tungstates, and that there may be three corresponding classes of phospho-molybdates. I shall discuss this question carefully in my paper. Meantime I may remark that all known methods of determining phosphoric oxide  $\text{P}_2\text{O}_5$  in the phospho-tungstates give results which are usually a little too low, as may easily be proved by qualitative tests. In consequence of the very high atomic weight of  $\text{WO}_3$  the determination of the  $\text{P}_2\text{O}_5$  must be extremely accurate to permit of much use of the method of computed ratios in assigning correct formulas.

My expectations as regards the possibility of generalizing results just obtained have been fully realized. Thus I have obtained finely crystallized antimonio-tungstates, and also antimonio-molybdates of sodium, potassium and ammonium. The analyses of the corresponding manganese salts agree well with the formulas,



but these must be regarded as provisional only. Quantitative separations of tungsten and molybdenum from arsenic, antimony, vanadium, &c., present wholly new problems in analytical chemistry, and I have spent much time in effecting their solution. In like manner I have obtained splendidly crystallized vanadio-tungstates and vanadio-molybdates of potassium, sodium and ammonium. These salts have a fine orange color and are readily soluble in water, crystallizing only from syrupy solutions. I have, to say the least, reason to believe in the existence of similar salts containing  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ , but in all these cases, as well as with the compounds of  $\text{PtO}_2$ ,  $\text{IrO}_2$ , &c., the chief difficulty consists in obtaining saturated salts, that is, salts in which  $\text{WO}_3$  or  $\text{MoO}_3$  have taken up all the deutoxide or pentoxide necessary to form a saturated compound. Add to this analytical and other difficulties and the task becomes a very formidable one, for which much time, labor and patience will be necessary.

CAMBRIDGE, March 5th, 1879.

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## ON NITROGEN IODIDE.

By J. W. MALLET.

The various researches upon the highly explosive black substance formed by the action of iodine upon ammonia have, as is well known, led to different views of its composition. That first put forward by Colin and Gay Lussac, namely that it is nitrogen tri-iodide, appeared to have been set aside by the experiments of Serullas,\* Millon,† Bineau,‡ Gladstone,§ Playfair, and Bunsen,|| all of whom found hydrogen to be a constituent,

\* Ann. Ch. Phys. [2] 42; 200 (1829).

† Ann. Ch. Phys. [2] 69; 78 (1838).

‡ Ann. Ch. Phys. [2] 70; 270 (1838) and [3] 15; 71 (1845).

§ Chem. Soc. Q. Jour. 4; 34 (1851).

|| Ann. Ch. Pharm. 84; 1 (1852).

but in varying amount, the formulæ  $\text{NHI}_2\text{—NH}_2\text{I—NH}_3\text{.NI}_3\text{—}$  and  $\text{NH}_3\text{.4NI}_3$  having been assigned to the products obtained by somewhat different processes, until more recently Stahlschmidt\* has revived the statement that under certain conditions at least the simple tri-iodide is formed.

One source of error in the analysis of this instable compound seems to have received insufficient attention from some of those who have examined it, and somewhat affects the conclusions drawn from the experiments of others. The substance, obtained as a black powder by the action of iodine on ammonia, decomposes gradually in contact with water, nitrogen gas being slowly evolved, iodine liberated, and iodic and hydriodic acids or ammonium salts formed. This decomposition takes place to no inconsiderable extent during the drying of the powder at ordinary temperature, and may be readily proved to have occurred by treating the dry residue with any of the solvents for iodine, as for instance alcohol, chloroform, or carbon di-sulphide, which at once form deeply coloured solutions. Hence the air-dried powder is really a mixture of the original substance or substances with various decomposition products, and so is unsuited for accurate analysis. On the other hand it might be doubted in regard to the analyses made of freshly prepared and still moist iodide, whether the results apply to a substance capable of being obtained in the dry state without decomposition.

Millon and Bineau, it is true, seem to have aimed at guarding against this difficulty by drying the material, side by side with solid potash, under a jar of gaseous ammonia. Bineau remarks that some of the gas is at first absorbed by the water moistening the powder, but that as the drying proceeds the gas recovers ("à peu près") its original volume, and that so moisture is gotten rid of without the iodide being decomposed. But, without qualitative examination of the gas, or a very accurate determination of its volume, this does not afford satisfactory proof that the dry substance is unchanged. I have observed continuous, though slow, evolution of little bubbles of nitrogen from the freshly prepared powder *when kept under strong aqueous ammonia*, though in this case no free iodine can be found, since as fast as it is liberated it reacts with the ex-

\* Pogg. Ann. 119; 421 (1863).

cess of ammonia, reproducing the nitrogen iodide, and forming more ammonium iodide, which latter therefore tends to accumulate in the liquid, and is thus to be found in the residue from drying up a moist mass of the powder in an atmosphere of ammonia.

I have applied a different method, which is often useful under other circumstances, for quickly getting rid of water, namely, repeated and rapid washing with absolute alcohol, followed by ether, and final evaporation of the last-named volatile liquid.

20 or 30 grms. of iodine was dissolved in a minimum of 95 per cent. alcohol, and precipitated by pouring into a large volume of cold water. The finely divided iodine was washed several times by decantation, then gently triturated for several minutes in a porcelain mortar with a large excess of the strongest liquid ammonia kept at or below  $0^{\circ}$  C. by a freezing mixture, the liquid poured off from the easily subsiding black powder, and replaced two or three times by fresh solution of ammonia. The powder was then at once transferred to a corked flask, and shaken up repeatedly, first with alcohol of 95 per cent., then with absolute alcohol, and finally with anhydrous ether, all of these liquids being artificially cooled. Most of the last portion of ether, which, as well as several of the preceding washings, was perfectly colourless, having been decanted off, the fluid black mud was turned out upon a filter, drained in a few moments, and the remains of the ether swept away as vapour by placing the filter and contents under a receiver and drawing cold dry air through in a rapid stream. This use of alcohol and ether to remove water from the iodide after its formation is not to be confounded with the employment by several experimenters of alcoholic solutions of iodine or ammonia, or both, in *making* the substance in the first instance.

The product thus obtained was explosive in the highest degree, yielding to very slight friction upon paper, frequently producing a crackling sound from little partial explosions when it was gently rubbed under water, and in two instances exploding in some quantity under water, with much violence and complete shattering of the vessel.

The relative quantities of nitrogen and iodine were ascer-

tained by decomposing an unweighed parcel of the substance by a moderately strong aqueous solution of sodium sulphite, neutralized by dilute sodium hydrate, and determining, in equal volumes of the liquid, the nitrogen as ammonia (expelled by boiling with excess of soda, and collected in sulphuric acid of standard strength), and the iodine as silver iodide.

A—In three experiments were obtained,

	No. 1	No. 2	No. 3	
NH <sub>3</sub>	.126	.184	.172	gram.
Equiv. to N	.104	.152	.142	"
Ag I	5.126	7.607	6.889	"
Equiv. to I	2.771	4.112	3.723	"

Nos. 1 and 2 refer to the same lot of material (separately decomposed, however); No. 3 to the product from a repetition of the same process.

These numbers correspond to,

	No. 1	No. 2	No. 3	Calc. for NI <sub>3</sub>
N (assumed)	14.	14.	14.	14.
I	373.02	378.74	367.04	381.

or, for 1 atom of nitrogen,

	No. 1	No. 2	No. 3
Atoms of iodine	2.94	2.98	2.89

B—Another specimen, similarly prepared, but with weaker ammonia, without any precaution as to cooling the materials used, and in a room the temperature of which was about 23° C., gave

	No. 1	No. 2	
NH <sub>3</sub>	.174	.152	gram.
Equiv. to N	.143	.125	"
Ag I	5.935	5.467	"
Equiv. to I	3.208	2.955	"

corresponding to,

	No. 1	No. 2
N (assumed)	14.	14.
I	314.07	330.96

or, for one atom of nitrogen,

	No. 1	No. 2
Atoms of iodine	2.47	2.61

C—Two other specimens, washed at first, not with alcohol and ether, but simply with water until no free ammonia could be detected in the washings, then kept under water for two or three days at ordinary temperature, with occasional stirring,

and finally dried after washing out with absolute alcohol and ether, as above described, gave

	No. 1	No. 2	
NH <sub>3</sub>	.136	.127	grm.
Equiv. to N	.112	.105	"
Ag I . . . .	3.954	3.667	"
Equiv. to I	2.137	1.982	"

corresponding to,

	No. 1	No. 2
N (assumed)	14.	14.
I . . . . .	267.12	264.27

or, for 1 atom of nitrogen,

	No. 1	No. 2
Atoms of iodine	2.10	2.08

Of the above results,

A distinctly represents the atomic ratio N : I = 1 : 3, fully confirming Stahlschmidt's conclusion that the tri-iodide can be obtained quite free from hydrogen.

B corresponds well with N : I = 2 : 5, and

C with the proportion found as the result of several earlier experiments, N : I = 1 : 2.

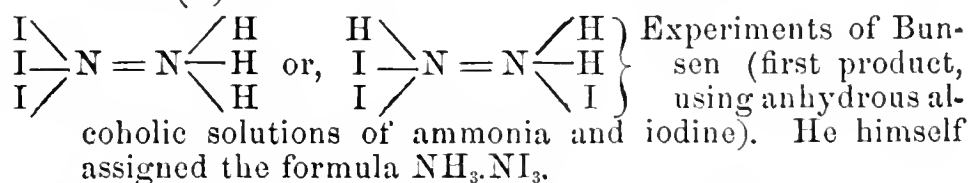
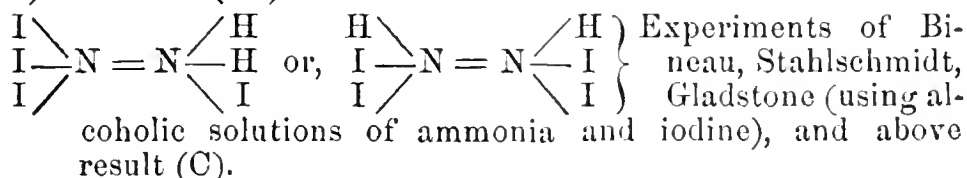
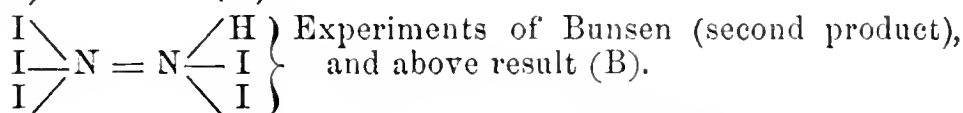
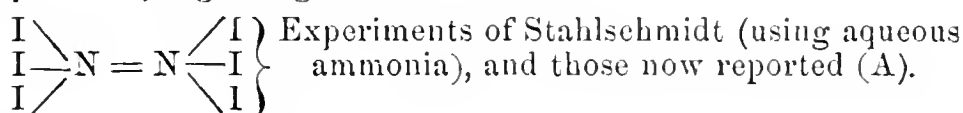
If B be admitted to stand for a definite compound, and not a mere mixture of A and C, which is rendered probable by the fairly close agreement of the results obtained with the calculated figures, there must be two atoms of nitrogen in the molecule, and the formula will be N<sub>2</sub>HI<sub>5</sub>. This formula may almost as well be deduced from Bunsen's analysis of one of the products he obtained (by addition of ammonia to a solution of iodine in nitro-hydrochloric acid, diluted with water, and rapidly washing with cold water) as that which he has himself assigned, viz. NH<sub>3</sub>.4NI<sub>3</sub>, since the figures stand

Calc. for N <sub>2</sub> HI <sub>5</sub> .	Calc. for NH <sub>3</sub> .4NI <sub>3</sub> .	Found by Bunsen.	
N 4.22 . . . .	4.38 . . . .	.008143 or, assumed 4.38	
H .15 . . . .	.19 . . . .		
I 95.63 . . . .	95.43 . . . .	.174417	93.82*
<hr/> 100.	<hr/> 100.		

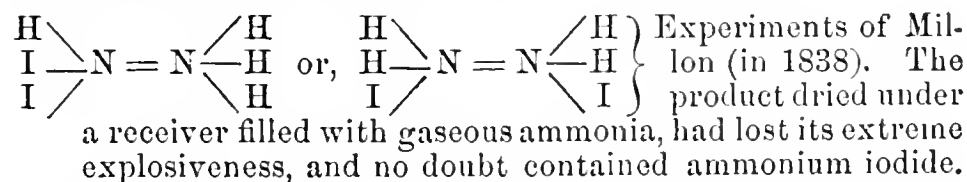
\*There seems to be an error in the calculation of the percentage of iodine in the original paper (Ann. d. Ch. n. Pharm.; 84; 1), but the figures here given are correctly deduced, I believe, from the actual weighings quoted, viz. .1300 grm. of ammonio-chloride of platinum and .0732 grm. of palladium.

It will be seen that the figures of the formula now proposed differ less from those of Bunsen's formula than the latter do from the results of experiment.

In view of the general fact that the compounds of nitrogen in which this element behaves as a pentad are those in which instability is chiefly observable, and noticing the various proportions in which iodine and hydrogen have been found together united with it, it seems fairly probable that the molecule of each of these explosive compounds contains two pentad nitrogen atoms; and reviewing all that has been published on the subject, with attention to the sources of error connected with the various methods used, we seem to have established the existence of the following series of substituted products, beginning with the tri-iodide:



It is much more doubtful whether we should add,



It appears that, not only may these different products be obtained by varying the conditions under which the formation of the explosive substance is effected, but during its decomposition by water, certainly involving more than a single series of reactions, one of these products may be more or less converted into others.

UNIVERSITY OF VIRGINIA, Feb. 21, 1879.

## DISCUSSION OF THE WORKING HYPOTHESIS THAT THE SO-CALLED ELEMENTS ARE COMPOUND BODIES.\*

BY J. NORMAN LOCKYER, F. R. S.

The author has been engaged for the last four years in preparing a map of the solar spectrum on a large scale, the work including a comparison of the Fraunhofer lines with those visible in the spectrum of the vapor of each of the metallic elements in the electric arc.

The first thing to be accomplished was the purification of the spectra, that is, the determination of which lines properly belonged to the spectrum of any given element and which ones were really due to impurities. When, for instance, an impurity of manganese was searched for in iron, if the longest line of manganese was absent the short lines must also be absent, on the hypothesis that the elements are elementary; if the longest line was present then the impurity was traced down to the shortest line present.

In the case of iron the final reduction showed coincidences between the short lines of the spectrum of this element and the short lines of a large number of other elements. Among these elements are vanadium, uranium, zirconium, yttrium, platinum, &c. In a table given in the original article it is shown that the line 3906 of the iron spectrum coincides with a line of uranium, yttrium and zirconium. There are also two other lines of uranium, viz. 3934 and 3954; two of yttrium, viz. 3947 and 3962; and one of zirconium, viz. 3965, all of which coincide with known short iron lines. So also in the case of titanium coincidences are noticed between the lines of this element and those of zirconium, manganese, cerium, didymium, &c.

The final reduction of the spectra of all the metallic elements in the region 39-40 showed that the hypothesis that identical lines in different spectra are due to impurities is not sufficient.

\*Abstract of a paper read before the Royal Society, Dec. 12, 1878 (*Amer. Jour. Sci.*, vol. xvii. p. 93).

For we find short-line coincidences between many metals the impurities of which have been eliminated, or in which the freedom from mutual impurity has been demonstrated by the absence of the longest lines.

The author had previously been led, through considerations in solar and stellar physics, to the hypothesis *that the elements themselves, or at all events some of them, are compound bodies*; and now as the old hypothesis that the elements are elementary led only to confusion, it was determined to try the application of the new one to the facts observed.

Obviously the first thing to be done was to inquire whether the hypothesis would explain these short-line coincidences. Calling, for sake of simplicity, the short lines common to many spectra *basic lines*, the new hypothesis, to be of any value, should present us with a state of things in which basic molecules representing bases of the so-called elements should give us their lines, varying in intensity from one condition to another, the *conditions* representing various compoundings.

Suppose A (nickel, let us say) to contain B (cobalt) as an impurity, and as an element, what will be the difference in the spectroscopic result?

A in both cases will have a spectrum of its own.

B as an impurity will add its lines according to the amount of impurity, as has been shown in previous papers.

B as an element will add its lines according to the amount of dissociation, as has also been shown.

The difference in the phenomena, therefore, will be that, with gradually increasing temperature, the spectrum of A *will fade*, if it be a compound body, as it will be increasingly dissociated, and it *will not fade* if it be a simple one.

Again, on the hypothesis that A is a compound body, that is, one compounded of at least two similar or dissimilar molecular groupings, then the longest lines at one temperature will not be the longest at another, the whole fabric of "impurity elimination," based upon the assumed single molecular grouping, falls to pieces, and the origin of the basic lines is at once evident.

Now to apply this reasoning to the dissociation of a known compound body into its elements.

A compound body, such as a salt of calcium, has as definite

a spectrum as a simple one; but while the spectrum of the metal itself consists of lines, the number and thickness of some of which increase with increased quantity, the spectrum of the compound consists in the main of channelled spaces and bands which increase in like manner.

In short, the molecules of a simple body and a compound one are affected in the same manner by quantity in so far as their spectra are concerned; *in other words, both spectra have their long and short lines*, the lines in the spectrum of the element being represented by bands or fluted lines in the spectrum of the compound; and in each case the greatest simplicity of the spectrum depends upon the smallest quantity, and the greatest complexity (a continuous spectrum) upon the greatest.

The heat required to act upon such a compound as a salt of calcium so as to render its spectrum visible, dissociates the compound according to its volatility; the number of true metallic lines which thus appear is a measure of the quantity of the metal resulting from the dissociation, and as the metal lines increase in number the compound bands thin out.

It has been shown in previous papers how we have been led to the conclusion that binary compounds have spectra of their own, and how this idea has been established by considerations having for a basis the observations of the long and short lines.

It is absolutely similar observations and similar reasoning which will be brought forward in discussing the compound nature of the chemical elements themselves.

The author now discusses certain phenomena observed in connection with the element calcium which show that the spectrum of this element undergoes changes under the influence of rising temperature, and that these changes are similar to those which the spectrum of a salt of calcium undergoes under similar conditions. As this case is fully considered in the following article,\* it is unnecessary to take it up here.

The spectrum of iron may be described as a very complicated spectrum, so far as the number of lines is concerned, in comparison with such bodies as sodium and potassium, lead, thallium, and the like, but unlike them again it contains no one

\* P. 15.

line which is clearly and unmistakably reversed on all occasions. Compared, however, with the spectrum of such bodies as cerium and uranium the spectrum is simplicity itself. Only a very small part of the spectrum is here considered, viz. the portion between H and G. Among the lines there are two triplets, two sets of three lines each; and the facts indicate that these two triplets are not due to the vibration of the same molecular grouping which gives rise to most of the other lines. The facts are as follows: In many photographs in which iron has been compared with other bodies, and in others again in which iron has been photographed as existing in different degrees of impurity in other bodies, these triplets have been seen almost alone, and the relative intensity of them, as compared with the few remaining lines, is greatly changed.

Further, in solar storms, as is well known, the iron lines sometimes make their appearance in the chromosphere. Now, if we were dealing here with one molecular grouping, we should expect the lines to make their appearance in the order of their lengths, and we should expect the shortest lines to occur less frequently than the longest ones. But precisely the opposite is the fact, as has been shown by Young in his observation of the chromospheric lines, made at Sherman, in the Rocky Mountains.

The question next arises, are the triplets produced by one molecular grouping or by two? The facts also help us to answer this question. It may be stated by way of reminder that in the spark photograph the more refrangible triplet is barely visible, while the one near G is very strong. Now, if one molecular grouping alone were in question this relative intensity would always be preserved, however much the absolute intensity of the compound system might vary; but if it is a question of two molecules, we might expect that in some of the regions open to our observations we should get evidence of cases in which the relative intensity is reversed or the two intensities are assimilated. What might happen does happen: the relative intensity of the two triplets in the spark photograph is grandly reversed in the spectrum of the sun. The lines barely visible in the spark photograph are among the most prominent in the solar spectrum, while the triplet which is strong in that photograph is represented by Fraunhofer

lines not half so thick. Indeed, while the hypothesis that the iron lines in the region referred to are produced by the vibration of one molecule does not include all the facts, the hypothesis that the vibrations are produced by at least three distinct molecules includes all the phenomena in a most satisfactory manner.

Changes in the lithium spectrum have also been observed by Frankland and Tyndall. It has been shown that a blue line occurs in this spectrum at high temperatures and that its intensity increases as the temperature rises. In a postscript to a letter written by Frankland to Tyndall in 1861, the following passage is found: "I have just made some further experiments on the lithium spectrum, and they conclusively prove that the appearance of the blue line depends entirely on the temperature. The spectrum of lithium chloride, ignited in a Bunsen's burner flame, does not disclose the faintest trace of the blue line; replace the Bunsen's burner by a jet of hydrogen (the temperature of which is higher than that of the Bunsen's burner) and the blue line appears, faint, it is true, but sharp and quite unmistakable. If oxygen now be slowly turned into the jet, the brilliancy of the blue line increases until the temperature of the flame rises high enough to fuse the platinum, and thus put an end to the experiment."

Taking up, finally, the case of hydrogen, the author remarks that all the phenomena of variability and inversion in the order of intensity presented to us in the case of calcium can be paralleled by reference to the knowledge already acquired regarding the spectrum of hydrogen. He and Frankland showed that the whole complicated spectrum of hydrogen can be reduced to *one line in the green*, corresponding to F in the solar spectrum. The observations made during eclipses have shown that at the time when the hydrogen lines were most brilliant in the corona, the calcium lines were not detected; next, when, the hydrogen lines being still brilliant, the *h* line was not present (a condition of things which, in all probability, indicated a reduction of temperature), calcium began to make itself unmistakably visible; and finally, when the hydrogen lines are absent, they become striking objects in the spectrum of the corona. In regard to the *h* line Frankland and the author showed in 1869 that it only made

its appearance when a high tension was employed. It was absent from among the hydrogen lines during the eclipse of 1875. And now this evidence is strengthened by the remark that it is always the shortest line of hydrogen in the chromosphere.

Assuming then that the spectra of the elements change in the manner described, under the influence of rising temperature, a perfect continuity of phenomena is established on the hypothesis of successive dissociations, analogous to those observed in the cases of undoubted compounds.

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## ON LOCKYER'S "HYPOTHESIS THAT THE SO-CALLED ELEMENTS ARE COMPOUND BODIES." \*

By C. S. HASTINGS,

*Assistant Professor of Physics, Johns Hopkins University.*

This paper is a discussion of certain phenomena observed in the course of a long investigation of the solar spectrum and the spectra of the various elements. In the discussion, the writer is led to the conclusion that the facts observed are only reconcilable on the assumption that, at the highest attainable temperatures, the bodies known to the chemist as elementary are dissociated into other forms of matter less complex; and, as all elements are supposed to undergo this degradation at sufficiently high temperatures, the inference is, that the chemical elements themselves bear the same relation to some simpler form or forms of matter, that chemical compounds do to these elements.

The idea of such a relation is by no means new, but, as this is the first bit of experimental proof offered, it is of the

\*Am. Jour. Sci. Vol. XVII. p. 93; see also preceding article.

highest interest. We shall here examine the nature of this evidence.

The argument is founded on two classes of phenomena :

1st. Numerous coincidences in lines of iron and of titanium with those of many other elements, the metals mentioned being assumed as spectroscopically pure.

2d. Analogies between the character of spectra of the same vapor under varying circumstances, and the spectra of vapors known to be compound.

Clearly the vulnerable point in the deduction from the first class of phenomena is the assumption that the iron, for example, is spectroscopically free from the impurity which would yield the lines in question. Before any weight can be attached to the argument, this assumption must be justified. Lockyer's proof of this essential purity is the absence of the "long" lines which are asserted to be characteristic of the spectrum of the impurity under all circumstances. To thoroughly understand the significance of this reasoning we must define the term long line.

If we examine spectroscopically a limited volume of incandescent vapor, not uniformly luminous in all parts, we shall find a certain number of lines in the most brilliant portion which grows progressively less as we approach the less brilliant portion. If the image of this vapor be projected upon the slit of the collimator, and of such a size as not to entirely cover it, certain lines will be traced nearer the limit of the duller portion than others. These are the longer lines. Practically we can secure these conditions best by means of the electrical discharge between terminals of the substance, the spectrum of which we wish to study. These lines are almost always the most brilliant in the spectrum, the first to appear and the last to disappear under any modification of the experiment. Are they long simply because they are the more intense? *i. e.* do the short lines disappear in decreasing the intensity of the light merely because they fall below the value necessary to stimulate the retina or impress the sensitive plate? or, on the other hand, is there besides this evident difference of degree a physical difference of kind? If the first, Lockyer's proof is complete; if the second, the proof is defective and with it the conclusion.

If we examine the spectrum of incandescent hydrogen, sufficiently brilliant, we see three or four lines, by far the most prominent being the line in the red corresponding to the C line of the solar spectrum, and that in the blue-green of the same refrangibility as the F line: of these two the C line is much the more conspicuous. If this advantage in favor of C be due to its greater subjective intensity, we know from Fechner's law that it will be more apparent with diminution of the intensity of the source. We may readily subject this conclusion to the test of experiment, either by observing the light after reflection from some white screen, such as paper or plaster, which exerts no selective absorption, or better, by throwing an image of the electric discharge through hydrogen on the slit of the collimator by a lens, the aperture of which may be reduced at will. Clearly, by neither of these processes do we modify the nature of our light; but by either process we find that the F line alone survives after considerable diminution and is consequently the brighter line. But, if the relative lengths of any two spectral lines are determined beyond cavil they are these very two. As hydrogen is the characteristic and ever-present element in the chromosphere, it has been studied from the time that the spectroscope was first applied to the examination of this phenomenon, and from that time it has been recognized that the C line is the longer. This experiment\* then proves that an element may be present, giving a spectrum, but without its longest line. As a still more important deduction we see that a line may be "long," as defined above, from two different reasons; one, on account of greater intensity, the other a less evident cause which we shall discuss further on. As a matter of convenience we will style the former *persistent* lines and the latter the *long* lines proper. Evidently the *persistent* line does not always retain this property, but the long line, distinguished by a physical difference, is always long; *e. g.* F is the persistent line in our vacuum tube and probably at the base of the chromosphere; C is the persistent line higher up in the chromosphere and the long line everywhere. As Lockyer's method does not distin-

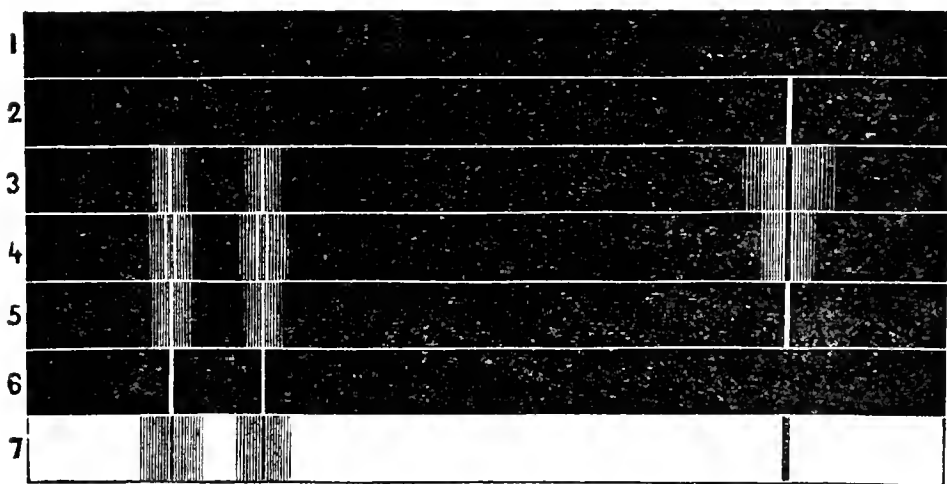
\*The experiment is but a less objectionable form of proof of what Huggins announced long ago when studying the spectra of nebulae, though its significance seems to have been overlooked. The "certain conditions of temperature and pressure" of Frankland and Lockyer which give F alone are simply such as give sufficiently small intensity of light.

guish between these two kinds of lines, but practically eliminates impurities only until those which were the persistent lines, under the conditions governing his observations of the impurity in question, have disappeared, his conclusions are unwarrantable.

We shall see farther on other instances of the distinction explained above, not less clear.

There remains one point in what precedes worthy of a moment's explanation. The C line is recognized as the most conspicuous in the hydrogen spectrum, but is proved not the most brilliant. This is no contradiction. This line occupies a place in that portion of the spectrum which alone is nearly saturated; the F line on the contrary falls very near that region which, by virtue of the properties of the retina, appears least saturated, whereas the more refrangible portion is lowered in saturation by the fluorescence of the media of the eye.

Of the phenomena of the second class, the only set complete in itself and in the discussion of which the reasoning is succinct and consecutive, is that relating to calcium. The accompanying figure with its description, taken from Lockyer's



The blue end of the spectrum of calcium under different conditions. 1. Calcium is combined with chlorine ( $\text{CaCl}_2$ ). When the temperature is low the compound molecule vibrates as a whole, the spectrum is at the red end and no lines of calcium are seen. 2. The line of the metal seen when the compound molecule is dissociated to a slight extent with an induced current. 3. The spectrum of metallic calcium in the electric arc with a small number of cells. 4. The same when the number of cells is increased. 5. The spectrum when a coil and small jar are employed. 6. The spectrum when a large coil and large jar are used. 7. The absorption of the calcium vapor in the sun.

paper, almost interprets itself. The author supposes up to 6 inclusive, that the only changes in appearance are due to change in temperature. Clearly, 2 is derived from 1 by a partial dissociation of the chloride, the former still exhibiting, it may be, the lines which were alone present in the latter. By analogy, Lockyer supposes 3 derived from 2 by partial dissociation of the element calcium. Here, doubtless, all the lines belonging to the chloride have disappeared, a result attained by simple increase of temperature. If the former reasoning is true we have only to increase our temperature until the element calcium is completely dissociated, when the line in 2 will vanish just as and for the same reason that the lines in 1 have vanished. This expectation we find justified in 6. Here we have, in our opinion, the strongest evidence which Lockyer has offered in favor of his hypothesis.

The phenomena, as far as discussed, are certainly explained by it, and in a simple manner. But let us see what points it leaves unexplained. In 3 we find one line reversed, the other two simple, while in 4 all are reversed. In 6 we find a temperature so high that the compound (calcium) cannot exist, but 7 asserts the existence of this compound in the sun, hence a lower temperature. That the temperature of the sun is below that of any artificial source is surprising, and was certainly heretofore thought improbable.

It is in the necessary deductions from this hypothesis, however, that we find its strongest objections. If the pair of lines to the left in the cut belong to a product of dissociation, then each one belongs to a different product, since they are separated occasionally in the chromosphere and always in the spectrum of Sirius. In the case of iron, even in the limited region 39-40, we must assume, according to Lockyer, three distinct products of dissociation. In hydrogen, by the same logical process we must, if we correctly apprehend the argument, assume not less than five products resulting from successive increase of temperature. Nor is there any indication that we are approaching an ultimate elementary form of matter which will put an end to indefinite complication, for none of these lines thus derived have the same refrangibility. But when we recognize that on this hypothesis we must count as many

distinct products as we can detect differentiations in spectral lines, the prospect is appalling, for this is only limited by the delicacy of our methods and the total number of lines in the spectra of all the elements.

Lockyer's explanation of the peculiarities of the calcium spectra is tenable only under the assumption that the essential differences are due solely to differences of temperature. May this assumption be granted? We think not. There is an all-important distinction between the discharge from an induction coil unmodified and when used with a condenser. To understand this distinction we must make clear to ourselves the process of discharge. The iron core of the coil is magnetized by the primary current; this current being arrested, the magnetism falls in intensity, not instantaneously, but the process occupies an appreciable time. The disappearance of the magnetism produces a difference of potential in the two termini of the coil proportional to the rapidity of the fall, which is most sudden at its beginning; if the termini are within striking distance a spark will pass, heating the insulating medium and thus lowering its resistance, so that the electro-motive force arising from the later and less rapid fall of magnetism in the core is still sufficient to overcome the lessened resistance. Thus the discharge occupies a large part of the considerable time necessary for the core to lose its magnetism. With a jar the process is quite different. Here a large amount of electricity must flow into the condenser before the potentials of the termini differ enough to disrupt the insulating medium, and when this condition is attained the core has lost the greater part of its magnetism, so the first discharge is not followed by a protracted, though decreasing current, as in the first case. Since the total amount of electricity passing in both cases is practically the same, and the heat evolved depends on the amount of electricity and the resistance, the temperature in the second case will clearly be much higher than in the first. Thus much is recognized and acted upon by spectroscopists. But suppose that besides heating intensely the medium through which the electricity passes, it be required to vaporize the material of the terminals, is there then no difference but temperature in the two cases? Most assuredly. The vaporizing of a metal is a process requiring

time as well as high temperature, and as the metal is hardly heated except at its point of contact with the heated gases of the spark, we must anticipate a much more copious evolution of vapor in the first case of slow discharge though of lower temperature. The characteristic envelope of metallic vapor about the spark of the unmodified discharge, absent or far less prominent in the condensed spark, is a familiar proof of this conclusion.

This long exposition of the nature of the electric discharge would be wholly unwarrantable did not the writer whose work we are examining, as well as other spectroscopists, seem to quite overlook its significance. Then too, we must make use of its conclusion in our reasoning.

We see then that 6, in the figure borrowed from Lockyer, represents the spectrum of calcium vapor, not only at a higher temperature than 2, but also at a less density, probably far less. It is not unlikely that the true cause of difference may be found in the latter fact.

Is it possible to explain all the phenomena cited by Lockyer, without introducing any hypothesis not rendered highly probable on other than spectroscopic grounds? Distinctly excepting the assumption that the line  $D_3$  of the chromosphere and the line 1474 of the corona are due to hydrogen, it is.

As the foundation of this explanation we suppose granted:

1st. The essential truth of the kinetic theory of gases.

2d. That molecules are practically elastic bodies capable of vibrating in several distinct periods, and imprinting oscillations of the same period on the luminiferous ether. This necessarily implies that vibrations in the luminiferous ether of these periods may set such molecules in oscillation.

Besides this we make the sole assumption that the "damping" of these vibrations varies in the different periods, *i. e.* that the time necessary to impart all the energy of vibration to the luminiferous ether varies with the different periods. This assumption can hardly be objected to; it is quite in keeping with the conduct of other elastic bodies which are more readily studied. A tuning-fork struck by a hard body may give out a non-harmonic overtone of greater subjective intensity than the fundamental tone, but left to itself the fundamental tone survives; a cord plucked by a sharp point gives a sound, the

quality of which changes speedily by the more rapid damping of certain of its partial tones.

According to the kinetic theory, a molecule of the vapor moves onward in an essentially straight line with a velocity proportional to the square root of the absolute temperature, until it comes into collision with another, when, in general, the velocity and direction of motion are changed, and a certain portion of the energy of motion is converted into vibratory motion within the molecule. The violence of the collisions, and consequently of the intermolecular disturbance, depends upon the average velocity of the molecules, that is upon the temperature; the frequency of collision depends upon the temperature and the density of the gas.

To fix our ideas, let us suppose a simple case of a gas whose molecules are capable of vibrating in two periods  $\alpha$  and  $\beta$ . Suppose again that the energy expressed in the vibrations of period  $\alpha$  is much more quickly imparted to the ether than that embodied in the period  $\beta$ , *e. g.* that  $\alpha$  would have its amplitude reduced to  $\frac{1}{10}$  in a unit of time, while  $\beta$  would suffer a reduction to  $\frac{9}{10}$  only. Now conceive this gas at such a temperature and pressure that the average interval of collision be this unit of time, the molecule would, on an average, yield 99 per cent. of its energy contained in the  $\alpha$  period to the ether, but only 20 per cent. of that in the  $\beta$  period. This proportion would obtain generally, for the energy in the  $\beta$  period clearly could not be cumulative, a collision tending to change the sign of vibratory motion nearly as often as to simply increase the amplitude. Seen in the spectroscope the line corresponding to  $\alpha$  would be by far the more intense; it would be the persistent line.

Imagine now, the temperature remaining the same, the density of the gas be so reduced that the average interval of collision be increased very many times. In this case the increase of energy of the  $\alpha$  form imparted to the ether is at best but one per cent., whereas the increase in that of the  $\beta$  form is very great. If now the gas be spectroscopically examined (supposing the volume of gas so arranged that as many molecules send light to the collimator as before),  $\alpha$  appears as before, but it has lost its position as the persistent line, for  $\beta$  is equally bright.

So much under the tacit assumption that the vibratory energy in  $\alpha$  and  $\beta$  are equal. Suppose, however, which, be it noted, is not mechanically improbable, that the energy in  $\beta$  is the greater; then by continuing the process of rarification we have the following phenomena: first,  $\alpha$  is the strong line, and tested as we tested hydrogen would prove the persistent line; second,  $\alpha$  and  $\beta$  would be equally intense, and, tested as before, neither would be called relatively persistent; finally  $\beta$  would be the more intense and also the persistent line. At all times  $\beta$  is the *long* line. On the other hand, if  $\alpha$  contains the greatest amount of energy it is always the most persistent as well as longest line.

Here we have derived a physical definition of a long line which may be thus stated:

The longer spectral line is that representing one of a molecule's possible vibrations which, on the average, corresponds to the greater energy.

As we have said above, Lockyer's method only determines the persistent lines under the limited range of conditions as regards temperature and pressure at his command. If to determine the long lines, the pressure be greatly reduced, the volume of the gas must be so inordinately increased, in order to secure sufficient intensity of light, that the experiment may be impossible. There is one case, however, in which we may have incandescent gases of extreme tenuity and enormous volume, namely, in the chromosphere of the sun. The relative distance, then, to which lines may be traced from the base of the chromosphere is a true expression of their relative lengths, provided that they are in the same region of the spectrum. Clearly this modification is necessary, for we may have a vibration of enormous energy to which the retina is not sensitive.

It will be seen from our point of view follows a ready explanation of the well known fact that the spectral lines increase in breadth with increased density in the gas, a phenomenon not easily explained, we think, on any other theory. Probably the period of molecular vibration, like that in other elastic bodies, is not independent of the amplitude of vibration. As the amplitude of vibration must depend on the violence of molecular collision, we should anticipate a greater proportion

of false light about a line with increased temperature. This asserts nothing about pressure. But if we recognize that the relative value of these false vibrations, since they would be rapidly damped, increases with the decrease of the mean interval of collision, the phenomenon observed follows as a necessity.

We will now as briefly as possible discuss the phenomena presented by Lockyer in the light of the preceding explanation.

The coincidences in the spectra of iron and titanium are due to impurities betrayed by long lines in the highly diluted vapors, which are not the persistent lines in the much denser vapors observed in the study of these impurities.

#### CALCIUM.

Referring to the cut, 1 and 2 are as explained; in 3 we have a large amount of vapor of considerable density, of which the centre is at a much higher temperature than the surrounding portion. At this density and temperature much of the light of the lower refrangibility is false in the sense defined above; but the colder molecules in the neighborhood readily take up the definite vibrations from the ether, and the line is reversed. The more refrangible lines are not reversed because the false light, though present, does not approach the lines in brilliancy, and thus though the lines are diminished in intensity by absorption, they are still relatively brilliant. In 4 however, by increased density of the vapor, and perhaps also by increased temperature, the lines are so widened and the colder vapor-envelope so increased in thickness that these lines are reversed in the centre. 5 requires no discussion. In 6 we have the vapor at a very high temperature, and at the same time very rare, from the nature of the discharge as explained above; the lines shown are the longest lines of the metal. Of these two the less refrangible has been proved by Young to be the longest. The observation of Huggins, which indicates that this is the only line in the spectrum of Sirius, is a proof that this vapor, copious in that star, is still extremely rare. Were these two lines due to different compounds, according to Lockyer, there is no more

reason why we should find H, the less refrangible, alone, than K, the more refrangible, but we may safely predict that the former may be found alone, or the two together, but K alone never.

#### IRON.

All the phenomena here discussed are explained in the simplest manner by the principles above announced. The lines observed in the chromosphere are really the long lines of the metal, at least the longest of that region of the spectrum, lines that are faint in the much denser gases studied by Lockyer because the molecule yields its energy, belonging to these periods, but slowly. If our author is driven, by the critical study of five lines, to the conclusion that iron vapor consists of no less than three elements or compounds, what may we expect when all the lines are as carefully studied?

#### LITHIUM.

As yet we have been able to find no difference between the blue and red lines of this metal, either by the discussion of the published observations, or of our own, except of luminous intensity; unless indeed one be reversed in the solar spectrum, which is more than doubtful. This difference in intensity becomes less marked at high temperatures in accordance with Fechner's law. The violet line is distinctly the longest, while the orange line is longer than the red. Yielding its vibrations more slowly to the ether, however, it becomes relatively prominent only at a very low vapor tension. The conditions required to make the latter line strong seem to have been met by the use of a coil and condenser.

In the cut illustrating the spectra of this metal there is probably a mistake in omitting the red and orange lines in the arc spectrum.

#### HYDROGEN.

The peculiarities of the F line have already been explained. The *h* line doubtless becomes relatively prominent only with extreme tenuity and high temperature. In the alloy of indium and this element, the compound being poor in hydrogen, we

expect, from Lockyer's researches on such bodies, that the relative density of the hydrogen vapor will be very small.

On the principles here expounded we find the origin of the numberless lines in the solar spectrum, not in unknown elements which are yet to be discovered, but in the long lines of known elements which are never the persistent lines in the conditions of density and limited volume at our command.

One more point with reference to the evidence of the stars. The hotter stars are probably less advanced in evolution, hence, probably have a greater equatorial velocity than our sun. In the sun the spectrum from the approaching side is more deflected, from the receding side less deviated; if we examine the spectrum from the whole surface at once with a high dispersive power, which practically we never do, the effect would be a widening of all the lines of the spectrum with a decreasing intensity in each, in other words, quite analogous to optical confusion as produced by spherical aberration. Hence the more delicate lines would disappear. In a star we can only observe the spectrum from the whole surface. Assuming a greater equatorial velocity in Sirius, and that its axis of revolution is not directed towards us, even if its spectrum closely resembles that of the sun it would appear as it does. This assumption explains the greater width of the hydrogen lines, which must otherwise be explained on assumed greater pressure, certainly not more probable. But we will not pursue this speculation further, though we might emphasize the fact that hydrogen, that element which, according to Lockyer, even at the limited means at our disposal, is readily split up into five or six different constituents, there, even at a temperature which, according to the same authority, destroys almost all other elements as we know them, still preserves the simplest form in which we know it in our laboratory and in the chromosphere!

*March 10th, 1879.*

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## ON A NEW VOLUMETRIC METHOD OF DETERMINING FLUORINE.

BY SAMUEL L. PENFIELD,

*Assistant in the Sheffield Laboratory.*

I have made the well-known reaction  $3\text{SiF}_4 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SiF}_6 + \text{SiO}_2$  the basis of a volumetric determination of fluorine, estimating the quantity of hydrofluosilicic acid formed from a given weight of a fluoride by means of a standard alkali solution.

It is impossible to titrate the hydrofluosilicic acid directly, because as soon as an alkaline reaction is reached the silicofluoride is decomposed and an acid reaction is indicated, which change goes on slowly. But when barium chloride and an equal volume of alcohol are added to the solution, barium silicofluoride is precipitated from the solution, and an equivalent amount of hydrochloric acid is liberated, which can be titrated; by this means, using litmus as an indicator, I was enabled to get some very satisfactory results, but the turbidity caused by the barium silicofluoride interfered with the change of color of the litmus, and cochineal I was not able to use at all.

On further experimenting I found that potassium chloride possessed some advantages over barium chloride. On adding potassium chloride and an equal volume of alcohol, potassium silicofluoride is precipitated from the solution, and an equivalent of hydrochloric acid is liberated, but the potassium silicofluoride is a very transparent precipitate, and does not interfere with the change of color of the indicators. It is necessary that alcohol shall make up at least one-half the volume of the liquid to be titrated, so as to precipitate the potassium silicofluoride as completely as possible.

The apparatus needed is very simple, and consists of a gasometer of ten or more litres capacity, a few flasks of about 150 c. c. capacity, a few large plain U-tubes 18 centimeters long and  $2\frac{1}{2}$  centimeters diameter, made without any narrowing in the bend, and a heavy iron plate supported properly so that it may be heated with a lamp.

The fluoride is weighed out accurately into one of the flasks ; unless it is a silicate, ten grams of powdered and ignited quartz are added, and two or three pieces of quartz about the size of kidney beans. These last facilitate mixing up the powder when the flask is shaken. The contents of the flask are then drenched with from 30 to 40 c. c. of sulphuric acid which has been previously heated and allowed to cool. The flask is tightly closed with a doubly perforated cork ; from the gasometer dry air is passed into the flask by means of a glass tube which reaches nearly to the bottom. The silicon fluoride mixed with air passes from the decomposing flask first through a small U-tube, made from ordinary glass tubing, 5 millimeters in diameter, and kept cool by being placed in a beaker of cold water, then into one of the large U-tubes intended for decomposing the silicon fluoride and absorbing the hydrofluosilicic acid. The U-tube contains a solution of potassium chloride mixed with an equal volume of alcohol ; the escaping gas is made to bubble through this, and to insure complete decomposition a second smaller U-tube is attached to the first : the first tube absorbs nearly all the acid, the second contains only traces. The decomposing flask is supported on the iron plate ; by its side is placed a second flask containing sulphuric acid and a thermometer supported so that its bulb dips into the acid ; the lamp heating the plate is placed midway between the flasks, and the heat is regulated so that the temperature of the acid remains between  $150^{\circ}$  and  $160^{\circ}$  C.

The decomposition is continued two hours in ordinary cases, and during that time a continuous current of air is forced through the apparatus, amounting to from five to six litres for the two hours, while the contents of the decomposing flask are frequently agitated by shaking.

After the decomposition and aspiration are completed the contents of the U-tubes are titrated : for this purpose they may be transferred to a beaker, the tubes being rinsed with alcohol and water, or better, the acid may be titrated directly in the U-tubes. In order that the alcohol may make up one half the volume of the liquid after the titration is completed, add a few cubic centimeters of alcohol before titrating, or where fifteen or more cubic centimeters are to be added use a standard alkali one half of whose volume is alcohol. As the

separated silicic acid sticks to the sides of the U-tube, it is necessary to have prepared a glass rod bent a little at one end to scrape off and break up this silica.

I have found by experiment that a simple dry U-tube between the decomposing flask and absorbing tube is sufficient to condense any sulphuric acid that may go over from the heated acid.

When fluorine is to be determined in a mineral containing chlorine as in the case of an apatite, substitute for the empty U-tube one filled with fragments of pumice impregnated with perfectly anhydrous sulphate of copper. This will intercept any hydrochloric acid, and will also serve to condense any sulphuric acid vapor that may go over from the heated acid. The calculation is very simple. Every one equivalent of sodium carbonate equals one equivalent of hydrofluosilic acid or six of fluorine, hence the proportion :

Mol. wt. $\text{Na}_2\text{CO}_3$ .	Mol. wt. 6 F.	Amt. of $\text{Na}_2\text{CO}_3$ .	Amt. of F.
106	:	114	: :
			: $x$

Below will be found some results which I have obtained from pure fluorspar. The time of conducting the operation in every case was two hours, the amount of aspiration varied from four and one-half to six and one-half litres, and the indicator used was cochineal.

The first six were titrated with a dilute solution of ammonia, one cubic centimeter of which equalled .01242 grams of fluorine, the last four with a solution twice as strong and one-half of whose volume was alcohol.

Fluorspar.	Corresponding Weight of Fluorine.	Fluorine found.	Gain or Loss.	C. C. of Air Aspirated.
.2464	.1200	.1199	— .0001	4500
.1804	.0879	.0895	+ .0016	5000
.2039	.0993	.0989	— .0004	5500
.2384	.1161	.1169	+ .0008	5000
.2074	.1010	.1023	+ .0013	6500
.2147	.1046	.1064	+ .0018	5500
.9292	.4325	.4329	+ .0004	5500
.4673	.2277	.2283	+ .0006	6500
.9901	.4824	.4817	— .0007	6000
1.0130	.4935	.4923	— .0012	6500

*March 3, 1879.*

PRELIMINARY NOTICE OF AN INVESTIGATION  
ON "PETROCENE," A PRODUCT OF THE  
DESTRUCTIVE DISTILLATION OF  
PETROLEUM.\*

BY SAMUEL P. SADTLER AND H. G. MCCARTER.

In the number of *Comptes Rendus* for 16th December last (tome 87, p. 991), which has just come to our notice, appears an article by MM. L. Prunier and R. David, entitled, "sur la nature de certains produits cristallisés, obtenus accessoirement dans le traitement industriel des pétroles de Pennsylvanie."

In this article the authors announce that they have begun an investigation of "Petrocene," a solid residue from petroleum, which they obtained from Dr. H. Tweddle, of Pittsburg, Pennsylvania. They give some general statements as to the several hydrocarbons, the presence of which they consider to have been indicated by the determinations they made of fusing points, boiling points, solubilities, together with crystallizations gotten with picric acid, and with binitroanthracene. Judging in this way, they state that anthracene, phenanthrene, chrysene, chrysogen and other hydrocarbons are present. They give no specific figures of analyses, but say merely that the percentage of carbon varied in their different analyses from 88 to 96 per cent. in 100. After propounding some interesting theories, based upon these indications, they close by promising to communicate the results obtained from a farther study of the subject, if, as they hoped, these should be new.

This same material has been the subject of our investigation for several months past, and we have obtained results which, while not as yet complete, are so far advanced as to be beyond the point of Messrs. Prunier and David's work, as it is stated in their article. We would therefore claim equal right to the field as scientific workers, and shall continue our studies, and hope to push them to an early completion.

\* Read before the American Philosophical Society, February 7th, 1879. Communicated by authors,

The material we have operated on consists of a full set of Dr. Tweddle's preparations, as described by him in the *Franklin Institute Journal*, Vol. 72, p. 204, which was given to one of us some two years ago, by Dr. F. A. Genth, and a bottle of the crude distillate before treatment with petroleum benzine, given to us by Dr. G. F. Barker.

Some weeks of study had indeed been given to these products in the summer of 1877, by one of us in conjunction with Dr. E. F. Smith, of the University of Pennsylvania, which work was interrupted and only resumed as stated, a few months ago.

The following is a brief and general statement of the ground covered by our work. The conclusions are all subject to revision as the examination of purer products may demand.

We found that the method of breaking up the compound by treatment with solvents did not suffice to give us pure products of constant compositions. We therefore availed ourselves of the method of forming double crystallizations with picric acid from solution in alcohol and benzol. We obtained what appeared to be three distinct crystallizations here, two of deep red crystals and one of brown plates. These were picked apart as they crystallized together, using a hand lens, and exercising great care, and were then submitted to recrystallizations until quite pure and distinct. On breaking up these picric acid compounds with dilute ammonia, we obtained at least two well-marked and distinctly different hydrocarbons. With regard to the hydrocarbon from the third set of crystals we are still in doubt.

Of the two hydrocarbons, one fuses constant at  $280^{\circ}$  C., and the other at  $178^{\circ}$  C. We are not able to identify them certainly with any of the known hydrocarbons.

Of both of these hydrocarbons, quinones have been made, and of one of them the alizarine, acting upon the quinone with strong sulphuric acid with heat, and then fusing the dried residue with solid potassium hydrate. The quinone from the hydrocarbon, fusing at  $280^{\circ}$ , dissolves in sulphuric acid with a dark purple color, and when the nearly black residue of disulphoquinonic acid and potassium hydrate are fused together, a dark yellowish-brown color is obtained. From the solution of this, hydrochloric acid precipitates the alizarine as a dark brown flocculent mass.

Several analyses of this quinone and of the alizarine were made. As we hold the whole subject still open to revision, we will not quote them, but merely say that both the quinone and the alizarine derived from the hydrocarbon, fusing at  $280^{\circ}\text{C.}$ , indicate a probable composition of  $\text{C}_{16}\text{H}_{14}$  for the hydrocarbon. This would be a dimethyl-anthracene, yet the hydrocarbon does not agree with the dimethyl-anthracene discovered by Van Dorp, and studied by Wachendorff and Zincke.

The analysis of the other quinone gives results approximating what would be demanded by mono-methyl-anthraquinone.

Undoubtedly both hydrocarbons are slightly contaminated with chrysene or some similar hydrocarbon of higher carbon percentage, from which it is exceedingly difficult to free them.

With this brief mention of the work done, we will defer any further discussion until our results are sufficiently advanced to be presented as a whole. We are now engaged upon the work, and will push it promptly to completion.

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## ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

### I.—INTRODUCTION.

BY IRA REMSEN.

A few years ago, in the course of an investigation on para-sulphobenzoic acid,\* I made some observations on the action of potassium pyrochromate and sulphuric acid on orthotoluenesulphonic acid and orthotoluenesulphamide, and on the corresponding compounds of the para-series, which led to the belief that the ortho-compounds are influenced by the oxidizing mixture less readily than the para-compounds. An exper-

\* Amer. Jour. Sci., Vol. V., 179, 274, 354; and Annalen der Chemie, 178, 275.

iment was made with a mixture of the two isomeric sulphonic acids, and it was shown that, after treating this mixture for a long time with an excess of the oxidizing agent, a product was obtained which, on being fused with potassium hydroxide, yielded a considerable quantity of salicylic acid; and the longer the oxidation was continued the larger seemed to be the proportion of salicylic acid obtained from the product by treating it with potassium hydroxide. After proving that no ortho-sulphobenzoic acid is formed in the experiment just referred to, the statement is made: "It seems indeed from this and a subsequent experiment that the ortho-acid is acted upon with much less energy than the para-acid, if acted upon at all."

The "subsequent experiment" may be described in the words of the article in question: "That the ortho-compound in the special case under consideration is acted upon less energetically than the para-compound was also shown in a rough way by the following experiment. The potassium salts of the two sulphotoluenic acids were separated very nearly by means of crystallization. The pure para-salt was introduced into the oxidizing mixture, and the reaction that ensued carefully observed. The same quantity of ortho-salt, still containing some of the para-salt, was afterward introduced into the same quantity of the oxidizing mixture as was employed in the former case, and the reaction compared with the former one. A striking difference was observed. Whereas the reaction commenced very quickly with the para-salt, and a strong evolution of gas took place; with the ortho-salt it was necessary to apply heat for a longer time before the reaction fairly began, and then the process was markedly more sluggish, a very slow evolution of gas continuing for a long time."

Again in the study of the two toluenesulphamides a similar difference was observed. The special experiment indicating this difference was described thus: "Orthotoluenesulphamide still containing some of the paramide, was subjected to oxidation. It was immediately noticed that, as in connection with the sulpho-acids, the action in this case was not as violent as in the case of the para-compound. After heating for some time the product was examined. The parasulphaminebenzoic

acid formed was filtered off and the filtrate extracted with ether. The ethereal extract, on being distilled, left behind a residue consisting of orthotoluenesulphamide with a very little parasulphaminebenzoic acid. The latter can be readily removed by redissolving the whole in water, adding a little alkali to the solution, and then extracting with ether. In this way absolutely pure ortho-amide can be obtained. This was again subjected to oxidation, and, after treating for a length of time, no new product could be discovered in the liquid—a portion of the substance only having been destroyed. Thus we see that the conduct of the ortho-amide is exactly analogous to that of the corresponding sulpho-acid.”

The results of the experiments just described led to the general inquiry whether the influence of a substituting-group, situated in the ortho-position with reference to a hydrocarbon residue, is such as always, either wholly or partially, to prevent the transformation of the residue into carboxyl by the chromic acid mixture. There are some cases on record which seem well adapted to throwing light upon this question. It has been shown, for instance, by Beilstein and Kreusler\* that, when nitroxylene obtained from ordinary xylene from coal-tar is oxidized, it yields a monobasic acid, nitro-toluic acid. This acid seems to have been obtained in a pure condition. At all events the fact was established very positively that this monobasic acid is not converted into a bibasic acid by further oxidation. The authors say: “Aus obigen Versuchen ergibt sich unzweifelhaft, dass die Einwirkung der Chromsäure auf Nitroxylol auf *eine* Methylgruppe beschränkt bleibt. Obgleich Toluylsäure durch Chromsäure mit der grössten Leichtigkeit kein Terephthalsäure uebergeht, widersteht die p-Nitrotoluylsäure dieser Einwirkung sehr kräftig. . . . In keinem Falle wird auch das zweite Methyl des Nitroxylols angegriffen. Die Bildung einer Säure von der Formel der Nitro-Terephthalsäure haben wir nicht beobachtet. Offenbar bewirkt der Eintritt negativer Elemente oder Radicale in den Kohlenwasserstoff, dass derselbe widerstandsfähiger gegen Oxydationsmittel wird. Aehnliche Erscheinungen finden sich häufig. So wird das *Dinitrotoluol* von Chromsäure nur äusserst wenig angegriffen, während *Nitrotoluol* dadurch leicht in p-Nitroben-

\* *Annalen der Chemie*, 144, 168.

zoensäure ueber-geht. Im *Xylol* werden beide Methylgruppen leicht oxydirt. Aber *Nitroxylol* und *Chlorxylol* liefern mit Chromsäure nur *p-Nitro-* und *p-Chlortoluylsäure*, und *Trichlorxylol* widersteht, nach den Versuchen des Herrn Vollrath der Einwirkung der Chromsäure auf das Vollständigste."

Vollrath's experiments are described\* a little later, and they show that parachlorxylene yields by oxidation parachlortoluic acid, and no bibasic acid; conducting itself just like the nitro-derivative.

Still later, Fittig, Ahrens and Mattheides in studying bromxylene showed† that it conducts itself towards chromic acid like the chlorine- and nitro-derivatives. They obtained a bromtoluic acid which, by further treatment with the oxidizing mixture, could not be converted into the corresponding bibasic acid.

It is perfectly clear from the examples referred to that the entrance of a substituting-group into xylene causes, at least sometimes, a remarkable change in the conduct of the substance towards the chromic acid mixture. One of the methyl-groups of the xylene is protected by the substituting-group against oxidation, while the other is apparently uninfluenced; and now the question would naturally arise: What position does the protecting group hold with reference to the protected methyl?

The results of my experiments on the sulpho-derivatives of toluene, as described above, would suggest that it is probably the methyl-group situated in the ortho-position which is protected in the compound, but before these experiments were performed there was nothing known that could lead to this suggestion, and no attempt indeed was made to offer any explanation of the phenomena under discussion, or to show any connection between all the cases on record in which a part of a molecule is protected from oxidation by the introduction of a negative group or groups.

After V. Meyer's‡ experiments had thrown light upon the compounds of the ortho-series, and had shown that many compounds, which had previously been considered as belonging to the meta-series, in reality belonged to the ortho-series,

\**Annalen der Chemie*, 144, 266.

† *Ibid.* 147, 32.

‡ *Ibid.* 156, 265.

Fittig\* called attention to certain peculiarities of the ortho-compounds, the most important one being the fact that "alle Ortho-verbindungen beim Behandeln mit chromsaurem Kalium und Schwefelsäure nicht die fuer die Meta- und Paraverbindungen charakteristischen Oxydationsprodukte liefern, sondern ganz zerstört werden." He says: "Vor Allem interessant aber scheinen mir die Versuche von Beilstein zu sein, der gefunden hat, dass auch die Orthosubstitutionsproducte des Toluols, das Orthochlortoluol, das Orthojodtoluol und das Orthonitrotoluol, welche von ihm noch als Metaverbindungen aufgefasst und beschrieben sind, beim Behandeln mit chromsaurem Kalium und Schwefelsäure keine substituirte Benzoesäuren liefern, sondern verbrannt werden." Reference is also made in this article to the conduct of salicylic acid as illustrating the conduct of ortho-compounds, but I showed† subsequently that not only salicylic acid but its isomeres, oxybenzoic and paraoxybenzoic acids conduct themselves exactly like salicylic acid, and, further, that instability towards chromic acid is a characteristic of a number of aromatic oxyacids—in fact of all that were examined by me.

The impression conveyed by Fittig's article is that ortho-compounds are *less stable* than the compounds of the other series, and, hence, his interesting observation does not assist us in explaining the cases above described in which *increased stability is the result to be explained*.

It will thus be seen that the subject of the influence exerted by substituting-groups upon hydrocarbon residues contained in the same compound, as indicated by the conduct of the compounds toward oxidizing agents, was, at the time the investigations now to be described were begun, almost entirely unexamined. And it was with the distinct object of showing whether, in those cases in which a part of a molecule is protected by the presence of a negative group, a common cause could be discovered, that the investigations were undertaken. The results thus far reached all agree, and they make the conclusion extremely probable that, *in all cases now on record in which hydrocarbon residues are shown to be protected from oxidation by the presence of negative groups, the latter are in the*

\*Zeitschrift für Chemie, N. F. VII, 179.

†In the article on parasulphobenzoic acid above referred to.

*ortho*-position with reference to the former; whereas oxidizable residues, situated either in the *meta*- or *para*-position with reference to the negative groups, are, under the same circumstances, transformed, just as if the negative groups were not present.

The oxidizing agent used, and the only one in connection with which the above conclusion holds good, is the common mixture of potassium pyrochromate, sulphuric acid and water. Other agents, such as nitric acid and potassium permanganate, act in an entirely different way, as is well known.

It is proposed then to present the results of the investigations which have led to the discovery of the principle embodied in the conclusion just stated; and, after these results have been presented, the connection between them, and their bearing upon the general subject under examination, will be discussed.

## II.—ON THE OXIDATION OF XYLENESULPHAMIDES.

BY IRA REMSEN AND M. W. ILES.

The first example selected for study was that afforded by the substitution-products of xylene. Instead of taking derivatives which had already been prepared, as the nitro-, chloro-, or bromo-derivatives, we selected, as probably better adapted to our purpose, the sulpho-compounds. As one of us had already shown that the amide of the sulphonic acid of toluene is readily oxidized, yielding a product which can be easily separated from the oxidizing mixture, and easily purified, it was thought probable that the sulphamides of xylene would be convenient substances to work with, and hence our attention was confined to these.

### *Preparation and Oxidation of the Amides.*

The specimen of xylene from which we started was obtained by us from coal-tar oil by careful fractional distillation. It was found to consist mainly of metaxylene—the proportion of the *para*-compound contained in it being much smaller than is common in crude xylene. The hydrocarbon was completely converted into sulphonic acids by gently heating it on the water-bath with concentrated sulphuric acid. The solution of

the sulphonic acids in water was converted into potassium salts, by first neutralizing with finely powdered chalk, filtering from precipitated calcium sulphate, adding a solution of potassium carbonate until a precipitate was no longer formed, then filtering again, and evaporating to dryness. The perfectly dry potassium salts were then treated with an equal weight of phosphorus pentachloride, the mass being kept cool during the operation. After the action of the chloride had ceased, strong aqueous ammonia was added, and, after cooling, the precipitated amides were filtered off.

As was anticipated, it proved to be an extremely difficult and tedious operation to obtain perfectly pure substances from this mixture. Nevertheless, we finally succeeded in proving that there were three distinct amides contained in it, two of which were derived from metaxylene, and the third from paraxylene. No special description of the details of the process of separation is necessary, as it simply consisted in successive recrystallizations. On first heating the mixture with water, a portion of it was converted into an oily looking liquid, while a larger portion passed into solution. The solution was filtered off, and the solidified oil again treated with hot water. Thus more of the solid amide was extracted from the liquid; and this was again filtered off and allowed to crystallize. The crystallized portions were together treated with hot water, and a further separation of the oily liquid obtained. Thus gradually the whole mixture was divided into two portions, one of which dissolved in hot water without first fusing, while the other passed into the liquid condition before the boiling point of water was reached, and then dissolved, though with difficulty, in the boiling water. By repeated crystallizations of these two portions, two comparatively pure products were obtained. The principal portion fused in pure condition at  $137^{\circ}$  (uncorr.) and the other portion at  $96-97^{\circ}$  (uncorr.)

Both of these substances had already been obtained by Jacobsen,\* and he had also shown that they are both derived from metaxylene. To show this, he heated them separately in sealed tubes with concentrated hydrochloric acid. Thus the sulphamide-group was removed and the hydrocarbon regenerated. By oxidizing this it was converted into isophthalic

\* *Annalen der Chemie*, 184, 179; and *Berichte d. deutsch. chem. Gesell.* X, 1009.

acid, and its nature thus determined. We performed the same experiments with the same results. There can hence be no doubt that two sulphamides can be obtained from metaxylene, one of them fusing at  $137^{\circ}$  and the other at  $96-97^{\circ}$ , and that the one with the higher fusing point is formed in much larger quantity than the other. For convenience, we may designate the former compound as  *$\alpha$ -xylenesulphamide*, and the latter as  *$\beta$ -xylenesulphamide*.

We mentioned above the presence of a third amide in the crude mixture. This substance was not formed in large quantity, and we did not succeed in preparing it in pure condition. It was found in the last mother-liquors from the crystallizations already described, and made its appearance in the form of verrucous masses without distinct crystalline structure. It fused at  $143^{\circ}$ , while according to Jacobsen\* the sulphamide of paraxylene fuses at nearly  $148^{\circ}$ . Although this amide was not prepared pure by us, we succeeded in showing beyond any doubt that it is in reality derived from paraxylene. By an indirect method, which will be described later, we transformed it into paratoluic and terephthalic acids, and showed that it can be completely changed into these bodies.

The above description refers to our main series of experiments. It must be remarked, however, that we experimented upon different specimens of xylene, and, while we always found the three amides mentioned, we also obtained in more than one instance a compound which differed from these three. This we believe to have been an amide from orthoxylene, as its fusing point corresponded very nearly to that given by Jacobsen for orthoxylenesulphamide. As we only desired to study the conduct of the amides towards the oxidizing mixture, we satisfied ourselves with the preparation of the three principal ones, and then subjected them to oxidation.

Some preliminary experiments were made with the impure amides for the purpose of determining whether they yielded acids by oxidation. The mixtures at first employed consisted almost entirely of the  *$\alpha$ -* and  *$\beta$ -*amides in varying proportions. Those portions which contained the largest proportions of the  *$\alpha$ -*amide were oxidized much more readily than those in which the  *$\beta$ -*amide was the principal constituent, in some cases the

\* Berichte d. deutsch. chem. Gesell. X, 1009.

oxidation took place with a violent evolution of gas, so that the vessel in which the operation was performed had to be cooled. In all these cases the oxidation was continued until the oil from the fused  $\beta$ -amide had disappeared from the surface of the oxidizing mixture. As a result of these preliminary experiments we found that a crystallized product is obtained by the oxidation of the mixtures, and that the quantity of this product varied according to the composition of the mixture. It was filtered off from the colored liquid, and washed out until the wash-water was colorless. It then appeared as a colorless, lustrous, crystallized body. It dissolved with evolution of carbon dioxide when treated with potassium carbonate, and was at least partially reprecipitated when the alkaline solution was acidified.

The formation of an acid or acids being thus established, it remained to show whether each of the amides had yielded an acid, or only one. The entire product was dissolved in dilute potassium carbonate, filtered and evaporated down to a comparatively small volume. Thus, if any of the amides should have remained unoxidized, they would crystallize out on cooling, while the sodium salt or salts, being presumably much more easily soluble than the amides, would remain in solution. In fact some amide did crystallize out. This was separated from the solution and was found to be nearly pure  $\alpha$ -amide. The solution of the sodium salt was then acidified and the precipitated acid carefully examined. It was soon found that it consisted of but one substance which could be recrystallized from water and from alcohol. Its fusing point was found to be  $247.5^{\circ}$ - $248^{\circ}$ ; and repeated crystallizations failed to change the fusing point. As will be shown below, this substance is a monobasic acid.

Some further experiments for the purpose of determining from which mixtures the largest yield of acid was produced. The yield was found to vary considerably even with the same mixture, but in general it was found that those mixtures which contained the largest proportions of  $\beta$ -amide yielded the largest quantity of the acid. This, taken in connection with the fact that, in a few cases in which a mixture containing a very large proportion of  $\alpha$ -amide was oxidized, scarcely any of the acid was obtained, led to the conclusion that the acid is derived

from the  $\beta$ -amide. The conclusion, however, was an erroneous one, as we subsequently discovered.

On subjecting perfectly pure  $\alpha$ -amide to the action of the oxidizing mixture, it was found to yield the monobasic acid which fuses at  $247.5^{\circ}$ – $248^{\circ}$ . The  $\beta$ -amide, on the other hand, is oxidized with much more difficulty, and its oxidation seems to take place in a different manner. Jacobsen mentions\* an acid which he obtained in very small quantity from the  $\beta$ -amide. In one experiment we also succeeded in obtaining a small quantity probably of the same acid. Its quantity, however, was so small as to make a careful examination of it out of the question. From the experiments performed by us we are inclined to the opinion that if the  $\beta$ -amide yields a monobasic acid by oxidation with chromic acid, this acid breaks up very easily under the further influence of the oxidizing agent. Unless this is so, it is difficult to explain the facts observed by us. How shall we, for instance, explain the fact, repeatedly established by our experiments, that a mixture containing a much larger quantity of  $\beta$ -amide than  $\alpha$ -amide yields by oxidation almost entirely, if not entirely, the acid of fusing point  $247.5$ – $248^{\circ}$ ? If the acid formed by oxidation of the  $\beta$ -amide corresponds in its properties to that formed by oxidation of the  $\alpha$ -amide, if it is stable towards the oxidizing mixture, then we must inevitably have obtained it in considerable quantities in the course of our investigations; for, from first to last, large quantities of the amides have been oxidized by us, and in many of our first experiments we used comparatively pure  $\beta$ -amide. We are hence compelled to reject the conclusion of Jacobsen that the oxidation of the two amides of metaxylene takes place in essentially the same way. We believe that there are fundamental differences between the two cases; and we believe that continued and more careful investigation will hence only serve to make these differences more apparent.

#### *Sulphaminemetatoluic Acid.*

Having shown that from a mixture of the two amides one acid is produced, and that this acid can be readily obtained in

\* Berichte d. deutsch. chem. Gesell., XI., 893.

pure condition, we prepared the new product in considerable quantity, and subjected it to careful study. Our method of procedure was this: The mixtures of amides were recrystallized a few times until, as already described, they were separated into a portion which fused under water, and a portion which did not liquefy on being heated under water. The portions of lower fusing point were first oxidized. The proportions used were: 22 grams amide, 106 grams potassium pyrochromate, and 160 grams concentrated sulphuric acid, diluted with three times its volume of water. This mixture is introduced into a flask connected with an inverted condenser, and then gently heated upon a sand-bath. In a short time an agitation is noticed on the surface of the liquid; now the flame is removed. The activity of the reaction increases, and proceeds for some time without the application of heat. When the liquid becomes quiet, heat is again applied, and the whole kept in gentle boiling for about twelve hours. The amount of time necessary to complete the oxidation varies with the composition of the mixture, so that no general directions can be given in regard to the time. In each case, it is safe to continue to apply heat until all the oil resulting from the fusion of the  $\beta$ -amide has disappeared from the surface of the oxidizing mixture.

After the process is completed, and the mixtures have cooled down, the product will be found in crystallized form. It is now filtered off and separated from unoxidized amides, by the method above described. It is dissolved in dilute sodium carbonate, filtered and evaporated down to a comparatively small volume. On cooling, the unchanged amide crystallizes out. Usually very little is obtained. The solution of the sodium salt of the acid is acidified with hydrochloric acid. The precipitated acid filtered and carefully washed with cold water, and then recrystallized from water.

After the oxidizing mixtures are filtered off, they still contain some of the new acid. A considerable quantity of this can be obtained by allowing the solutions to evaporate somewhat on the water-bath, when, on cooling, the acid will be deposited. There is still contained a small quantity of another acid in the concentrated oxidizing mixtures. This is not, however, as has been indicated, isomeric with the acid now specially

under consideration. As will be shown further on, it is a result of further oxidation of the first product.

After one or two crystallizations from water the new acid is perfectly pure. Its analysis showed it to have the composition,  $C_8H_9SNO_4$ .

I.—0.231 grams of the acid fused with potassium hydroxide and then treated with bromine water according to the method recently described by Fahlberg and Iles\* gave 0.252 grams  $BaSO_4 = 0.0345996$  grams S.

II.—0.28475 grams of the acid treated in the same way gave 0.30822 grams  $BaSO_4 = 0.042318$  grams S.

III.—0.2865 grams of the acid treated, according to Liebig's directions, with potassium hydroxide and saltpeter, gave 0.31497 grams  $BaSO_4 = 0.043245$  grams S.

IV.—0.44905 grams substance gave 27.2 cc. N at 759.5 mm. pressure, and  $24^\circ$  C.

V.—0.59615 grams substance gave 35 cc. N at 761.5 mm. pressure, and  $19^\circ$  C.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
$C_8$	96	44.65	...	...	...	...	...
$H_9$	9	4.19	...	...	...	...	...
$O_4$	64	29.77	...	...	...	...	...
N	14	6.51	...	...	...	6.78	6.75
S	32	14.88	14.98	14.86	15.09	...	...
	<hr/> 215	<hr/> 100.00					

The results of these analyses, taken together with those to be given of the salts of the acid, prove conclusively the correctness of the formula accepted.

The acid is hence seen to be derived from the amide by the oxidation of one of the methyl groups.

The amide being  $C_6H_3 \begin{Bmatrix} CH_3 \\ CH_3 \\ SO_2NH_2 \end{Bmatrix}$ , the acid is  $C_6H_3 \begin{Bmatrix} CH_3 \\ COOH \\ SO_2NH_2 \end{Bmatrix}$ .

As the xylene from which the amide is derived is meta-xylene, the acid which would be formed from it by the oxidation of one methyl-group would be metatoluic acid. Hence the name of the new acid is *sulphaminemetatoluic acid*.

\* Berichte d. deutsch. chem. Gesell. XI, 1187.

Sulphaminemetatoluic acid is comparatively easily soluble in hot water, but difficultly soluble in cold water. In hot alcohol it is easily soluble, in cold less readily, but still not difficultly. It is nearly insoluble in ether, both warm and cold. In cold chloroform it is insoluble, in warm but slightly. Finally in both warm and cold carbon bisulphide it is insoluble. From the solution in hot water it crystallizes on cooling in peculiar, thick, pointed, prismatic crystals which occasionally attain a considerable size. Sometimes it crystallizes in very long, lustrous, thick needles, but the two forms have exactly the same fusing point. The fusing point is  $247.5\text{--}248^\circ$  uncorrected, and  $254.5\text{--}255^\circ$  corrected.

A large quantity of the acid was prepared by us in perfectly pure condition. We took every precaution to insure its purity, and always carefully tested every portion used for different experiments. In order to characterize the acid a number of its salts were prepared and analyzed.

*Barium sulphaminemetatoluate*,  $(\text{C}_6\text{H}_3\text{SO}_2\text{NH}_2\text{CH}_3\text{COO})_2\text{Ba} + 5\text{H}_2\text{O}$ , was prepared by boiling the free acid with pure barium carbonate. It is very easily soluble, but from the concentrated solutions it separates in a compact mass which consists of very fine silken needles. The crystals dried in the air were analyzed.

I.—0.3865 grams dried salt gave 0.158 grams  $\text{BaSO}_4 = 0.092904$  grams Ba.

II.—0.157 grams dried salt gave 0.06475 grams  $\text{BaSO}_4 = 0.03807$  grams Ba.

III.—0.1815 grams salt lost 0.025 grams  $\text{H}_2\text{O}$  at  $200^\circ$ .

IV.—0.1360 grams salt lost 0.01888 grams  $\text{H}_2\text{O}$  at  $180^\circ$ .

	Calculated.		Found.			
	I.	II.	III.	IV.		
$(\text{C}_6\text{H}_3\text{SNO}_4)_2$	428		...	...	...	...
Ba	137	24.25*	24.04*	24.25*	...	...
5 $\text{H}_2\text{O}$	90	13.74	...	...	13.77	13.88
	655					

*Calcium sulphaminemetatoluate*,  $(\text{C}_6\text{H}_3\text{SO}_2\text{NH}_2\text{CH}_3\text{COO})_2\text{Ca} + \frac{1}{2}\text{H}_2\text{O}$ , was prepared by boiling a solution of the acid with finely powdered Iceland spar. It is easily soluble in water,

\*Calculated for dried salt.

and crystallizes in small concentrically arranged needles. After drying in the air, it was analyzed.

I.—0.3620 grams salt lost 0.0195 grams  $\text{H}_2\text{O}$  at  $200^\circ$ , and gave 0.101 grams  $\text{CaSO}_4$ .

II.—0.3145 grams salt lost 0.0170 grams  $\text{H}_2\text{O}$  at  $195^\circ$ , and gave 0.0875 grams  $\text{CaSO}_4$ .

Calculated.			Found.	
			I.	II.
$(\text{C}_8\text{H}_8\text{SNO}_4)_2$	428	86.47	...	...
Ca	40	8.08	8.21	8.18
$1\frac{1}{2}\text{H}_2\text{O}$	27	5.45	5.39	5.40
	495	100.00		

*Silver sulphaminemetatoluate*,  $\text{C}_8\text{H}_8\text{SO}_2\text{NH}_2\cdot\text{CH}_3\text{COO Ag}$ , was prepared by adding silver nitrate to a solution of the ammonium salt. It is precipitated in flocculent masses, which may, however, be obtained in the form of needles by recrystallization from water. The air-dried salt was analyzed.

I.—0.083 grams salt gave 0.02775 grams Ag.

II.—0.10125 grams salt gave 0.03375 grams Ag.

Calculated.			Found.	
			I.	II.
$\text{C}_8\text{H}_8\text{SNO}_4$	214	66.46	...	...
Ag	108	33.54	33.43	33.33
	322	100.00		

*Sodium sulphaminemetatoluate* is very easily soluble in water and crystallizes in delicate needles.

*Copper sulphaminemetatoluate*, prepared by precipitating the barium from a solution of the barium salt by means of copper sulphate, can be obtained, by careful evaporation, in delicate radiating needles of a blue color. If evaporated by boiling, the salt is partly decomposed, and a light blue, difficultly soluble powder is thrown down.

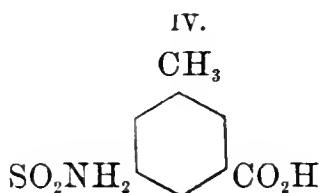
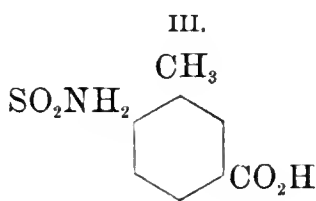
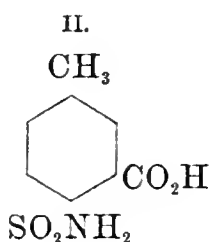
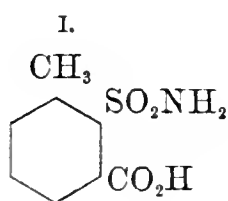
*Cobalt sulphaminemetatoluate* crystallizes in small round, very compact, radiating needles. It is easily soluble in water.

When heated with concentrated hydrochloric acid in a sealed tube up to  $220^\circ$  sulphaminemetatoluic acid is decomposed entirely with a separation of free carbon. At  $150^\circ$  it is also completely decomposed. Special experiments were under-

taken to determine the temperature at which the decomposition takes place. If the substance is not heated above  $130^{\circ}$ , the acid separates unchanged on cooling. If heated up to  $140^{\circ}$  decomposition takes place. It was not possible to obtain metatoluic acid from it by this means. Experiments with dilute hydrochloric acid gave similar results; no metatoluic acid could be obtained. It will be seen later that this conduct is entirely different from that shown by an isomeric acid, sulphamineparatoluic acid.

*Structure of Sulphaminemetatoluic Acid.*

For the purpose of this investigation it was of the first importance for us to determine, by the application of all of the methods at our command, the structure of the new acid. The method of formation leaves no doubt in regard to the relative positions of the methyl and carboxyl groups with reference to each other. They are in the position designated as meta. It remains, however, to decide in what relation the sulphamine-group stands to the two other groups in the benzene-nucleus. According to the commonly accepted hypothesis in regard to the nature of benzene-derivatives, four isomeric sulphamine-metatoluic acids are possible. These may be conveniently represented by the following schemes:



It must be borne in mind that the facts expressed by these formulas might be expressed equally well in ordinary language, and that the only object in using them here is for the sake of brevity. The proofs which will be offered for the structure of the acid under discussion are not dependent for

their validity upon the acceptance of any hypothesis. They would be equally valid no matter what hypothesis we might hold in regard to the nature of benzene and its derivatives.

On examining the formulas given, it will be seen that, in the first, the sulphamine-group is represented as occupying the same position with reference to both the other groups, and, as the carboxyl-group has undoubtedly been formed by direct oxidation of the original second methyl-group of the amide, in the latter compound the sulphamine-group must have occupied the same position with reference to both methyl-groups. The same statement holds true in regard to formula IV., and the original amide of the acid represented by it. It would seem probable that, if oxidation of either methyl should take place readily in these two amides, the second methyl would also be oxidized, and that in both cases the chief product of the oxidation would be a bibasic acid, while, of course, as an intermediate product, some of the monobasic acid resulting from oxidation of only one of the methyl-groups would probably be obtained. It is difficult, however, to speculate upon this subject. It is possible that the process would take place in an entirely different way. Possibly one of the methyl-groups might be oxidized completely at first, and then by its presence in the molecule prevent the further oxidation. There are some facts known which seem to point to this latter as the true view of the matter; but there are not enough facts known to warrant us in expressing anything like a decided opinion at present.

As regards formulas II. and III., the acids represented by them are derived from the same amide. If II. represents our acid, then the ortho-methyl group must have been oxidized and the para-methyl protected. But this would not be at all in harmony with the facts discussed in the introduction to this memoir. There is no case known in which a para-methyl group is protected from oxidation; and, further, when these investigations were begun there was no case known in which an ortho-methyl-group was oxidized by the chromic acid mixture. If, on the other hand, our acid has the structure represented by formula III., then the ortho-methyl has been protected and the para-methyl oxidized; and this would be in accordance with known facts. It will be shown that this formula actually represents the structure of our acid.

*Transformation of Sulphaminemetatoluic Acid into Oxytoluic Acid (Orthohomoparaoxybenzoic Acid).*

The conversion of the sulphamine-group,  $\text{SO}_2\text{NH}_2$ , into hydroxyl can be effected very readily. Indeed it seems to take place better than the same conversion of the sulpho-group. The potassium salt of sulphaminemetatoluic acid was made, and its solution evaporated nearly to dryness, so that, on cooling, it formed a pasty mass. This was then gradually added to about twenty parts fused potassium hydroxide, contained in a large silver crucible. The mass was kept in fusion by the aid of a small flame until ammonia ceased to be evolved, and during this time it was continually stirred with a silver spatula. After cooling, the contents of the crucible were dissolved in a relatively small amount of water, and the solution, which was almost colorless, acidified with dilute hydrochloric acid. A voluminous white precipitate was immediately formed, and sulphur-dioxide escaped. The precipitate, after being filtered off and carefully washed out with cold water, was dissolved in hot water in which it is quite easily soluble. On cooling, this solution deposited the new acid in beautiful, long, lustrous needles, which, in their general appearance, suggest salicylic acid. The acid exhibited the properties of a pure substance, such as crystalline form, constant fusing point, &c., and, hence, it was at once analyzed. On drying at  $100^\circ$  it was found to become opaque, and this change was shown to be due to the escape of water of crystallization.

0.2925 grams substance lost 0.0172 grams  $\text{H}_2\text{O}$  at  $130^\circ$ .

	Calculated.		Found.
$\text{C}_8\text{H}_8\text{O}_3$	152	94.41	...
$\frac{1}{2}\text{H}_2\text{O}$	9	5.59	5.88
	<hr/> 161	<hr/> 100.00	

0.1605 grams substance, dried at  $100^\circ$ , gave 0.07925 grams  $\text{H}_2\text{O}$ ; and 0.3700 grams  $\text{CO}_2$ .

		Calculated.		Found.
$\text{C}_8$	...	96	63.16	62.87
$\text{H}_8$	...	8	5.26	5.49
$\text{O}_3$	...	48	31.58	31.64
		<hr/> 152	<hr/> 100.00	<hr/> 100.00

The analyses thus show that the substance has the composition of an oxytoluic acid containing half a molecule of water of crystallization in its molecule. It is  $C_8H_8O_3 + \frac{1}{2}H_2O$ .

The acid is difficultly soluble in cold water, but easily in hot water. The solution is not colored by ferric chloride. It is easily soluble in alcohol and ether; insoluble in carbon bisulphide, cold as well as hot; insoluble in cold chloroform, difficultly in boiling chloroform. It crystallizes from water in long, beautiful, very fine needles with a silken luster. With its water of crystallization it melts at  $146.5^\circ$ - $147^\circ$  (uncorr.) After the loss of its water, its fusing point is  $170.5^\circ$ - $171^\circ$  (uncorr.), or  $174^\circ$ - $175^\circ$  corrected. The acid, after the water of crystallization is driven off, is brittle and without luster. It is not volatile with water vapor. It sublimes easily, and is deposited in the form of interlaced needles. These fuse at  $165^\circ$ - $166^\circ$ . The low fusing point indicates a slight decomposition under the influence of the heat.

*Calcium oxytoluate*,  $(C_6H_3.OH.CH_3.COO)_2Ca + 3H_2O$ , was prepared by boiling the acid with finely powdered Iceland spar. It is easily soluble in water, and crystallizes from a concentrated solution in small, spherical masses which are composed of microscopic needles.

I.—0.16825 grams salt lost 0.02307 grams  $H_2O$  at  $130^\circ$ ; and gave 0.581 grams  $CaSO_4$ .

II.—0.1177 grams salt lost 0.01605 grams  $H_2O$  at  $130^\circ$ ; and gave 0.0404 grams  $CaSO_4$ .

	Calculated.		Found.	
	I.	II.	I.	II.
$(C_8H_7O_3)_2$	302	76.26	..	...
Ca	40	10.10	10.16	10.09
$3H_2O$	54	13.64	13.71	13.64
	<hr/> 396	<hr/> 100.00		

*Barium oxytoluate*,  $(C_6H_3.OH.CH_3.COO)_2Ba + 3H_2O$ , was prepared by boiling the free acid with pure barium carbonate. It is not as easily soluble as the calcium salt. It crystallizes in spherical masses which have a mother-of-pearl luster.

I.—0.19675 grams salt lost 0.021 grams  $H_2O$  at  $120^\circ$ ; and gave 0.09325 grams  $BaSO_4$ .

II.—0.1604 grams salt gave 0.07585 grams  $\text{BaSO}_4$ .

III.—0.14275 grams salt lost 0.1525 grams  $\text{H}_2\text{O}$  at  $120^\circ$ .

IV.—0.235 grams salt lost 0.026 grams  $\text{H}_2\text{O}$  at  $155^\circ$ .

	Calculated.		Found.			
			I.	II.	III.	IV.
$(\text{C}_8\text{H}_7\text{O}_3)_2$	302	61.26	...	...	...	...
Ba	137	27.79	27.87	27.81	...	...
$3\text{H}_2\text{O}$	54	10.95	10.67	...	10.68	11.06
	<hr/>	<hr/>				
	493	100.00				

The barium salt is decomposed at  $160^\circ$ .

*Manganese oxytoluate*,  $(\text{C}_6\text{H}_3.\text{OH}.\text{CH}_3.\text{COO})\text{Mn} + 2\text{H}_2\text{O}$ , was prepared by boiling the free acid in water with manganese carbonate. It is very easily soluble in water, and crystallizes in small, compact prisms of a light brown color.

I.—0.19765 grams salt lost 0.01825 grams  $\text{H}_2\text{O}$  at  $160^\circ$ ; and gave 0.0391 grams  $\text{Mn}_3\text{O}_4$ .

II.—0.220 grams salt lost 0.02085 grams  $\text{H}_2\text{O}$  at  $160^\circ$ ; and gave 0.04325 grams  $\text{Mn}_3\text{O}_4$ .

	Calculated.		Found.	
$(\text{C}_8\text{H}_7\text{O}_3)_2$	302	76.85	...	...
Mn	55	13.99	14.25	14.16
$2\text{H}_2\text{O}$	36	9.16	9.23	9.48
	<hr/>	<hr/>		
	393	100.00		

*Copper oxytoluate*,  $(\text{C}_6\text{H}_3.\text{OH}.\text{CH}_3.\text{COO})\text{Cu} + 1\frac{1}{2}\text{H}_2\text{O}$ , was prepared by adding a solution of copper nitrate to a solution of barium oxytoluate. A flocculent, blue precipitate separates immediately. This precipitate dissolves in hot water, and, on cooling, the solution deposits beautiful, dark green, compact prisms. Sometimes by slow crystallization from a dilute solution, large groups of compact prisms are formed. The salt is difficultly soluble in water. It is the most characteristic of the salts of oxytoluic acid examined by us.

I.—0.143 grams salt lost 0.0102 grams  $\text{H}_2\text{O}$  on being heated up to nearly  $200^\circ$ .

II.—0.1113 grams dried salt gave 0.02265 grams  $\text{CuO}$ .

III.—0.1113 grams dried salt deposited 0.0184 grams metallic copper by the electrolytic method.

	Calculated.		Found.		
			I.	II.	III.
$(C_8H_7O_3)_2$	302	76.96	...	...	...
Cu	63.4	16.16	...	16.24	16.53
$1\frac{1}{2}H_2O$	27	6.88	7.13	...	...
	<hr/>	<hr/>			
	392.4	100.00			

*Silver oxytoluate* is precipitated as a flocculent mass on adding silver nitrate to a solution of the ammonium salt. If this precipitate be dissolved in water it is deposited, on cooling, in the form of beautiful compact crystals. This salt was not analyzed.

When treated with nitric acid the oxytoluic acid under consideration is converted into a yellow compound which can be obtained in crystallized form from a solution in water. This is probably a nitro-compound. As yet we have not studied any more derivatives of the acid.

[To be continued.]

## REVIEWS AND REPORTS.

ON AN APPLICATION OF THE NEW ATOMIC THEORY TO THE GRAPHICAL REPRESENTATION OF THE INVARIANTS AND COVARIANTS OF BINARY QUANTICS. By J. J. Sylvester. American Journal of Mathematics, Vol. I. p. 64.

There is a conviction in the minds of chemists, that at some future time, when the theory of chemistry shall have been developed, the intricate phenomena of the science will become expressible in the perfect language of mathematics, just as at present it is possible thus to express the phenomena of electricity, of light, of heat.

Hence any indication of the possibility of applying mathematics to the discussion of the problems of chemistry must be hailed with delight by those who are accustomed to think upon these problems.

As an indication of this kind we call attention to the extremely interesting article the title of which is given above. It is true the author does not himself propose to apply mathematics to chemistry, but, strange as it may sound, he proposes to make use of the common chemical formulas to express mathematical truths. The fact that this latter application is possible indicates, however, that there exists an analogy between certain facts which the mathematician desires to express and those which the chemist has to deal with.

The author's own language will more forcibly convey the idea which he has in mind than anything we can say:—"Impressed as I had long been with a feeling of affinity, if not of identity, of object between the inquiry into compound radicals and the search for 'Grundformen' or irreducible invariants, I was agreeably surprised to find, of a sudden, distinctly pictured on my mental retina a chemico-graphical image serving to embody and illustrate the relations of these derived algebraical forms to their primitives and to each other."

While we cannot pretend to a knowledge of the branch of mathematics to which reference is here made, we may by means of a few quotations make clear the character of the analogy thus discovered.

"Any binary quantic," says Professor Sylvester, "may be denoted by a single letter with a number attached corresponding to its degree, and may therefore be adumbrated by a chemical symbol, with corresponding *valence*. Thus hydrogen, chlorine, bromine, or potassium, will serve to denote so

many distinct binary linear forms; oxygen, zinc, magnesium, etc., binary quadrics; boron, gold, thallium, cubics; carbon, lead, silicon, tin, quatics; nitrogen, phosphorus, arsenic, antimony, etc., quintics; sulphur, iron, cobalt, nickel, etc., sextics.

"The factors of any algebraical form may be regarded as in some sense the analogues of the rays of atomicity in the equivalent chemical atom—these rays being what Dr. Frankland, according to his nomenclature, would have to designate as free bonds; such rays between two consecutive atoms in a molecule are conceived as blending in some manner so as to represent some unknown kind of special relation existing between them; they may then with propriety be called bonds or lines of connexion.

"An invariant of a form or system of algebraical forms must thus represent a saturated system of atoms in which the rays of all the atoms are connected into bonds. Thus *e. g.*  $O_2$  . . . will represent a quadratic invariant of a quadric. . . . Potash, . . . having for its graph  $K-O-H$ , will represent the invariant to a system of one quadratic and two linear forms which is linear in each set of coefficients."

The author illustrates the analogy by a number of examples. In speaking of the formula benzol, he says:—"As, however, the question is one purely of colligation or linkage in the abstract, it is sufficiently described as a hexagon in which the three pairs of opposite angles are joined; or, if we please, as two triangles, in which each angle of one is connected with a corresponding angle of the other. In regard of the atomicity theory, all these modes of colligation are identical, and the supposition that there is any real difference between them, or that figures in space are distinguishable from figures in a plane (as I heard suggested might be the case by a high authority, at a meeting of the British Association for the Advancement of Science, where I happened to be present) is a departure from the cautious philosophical views embodied in the theory as it came from the hands of its illustrious authors, and continued to be maintained by their sober-minded successors and coadjutors, and affords an instructive instance of the tendency of the human mind to the worship, as if of self-subsistent realities, of the symbols of its own creation."

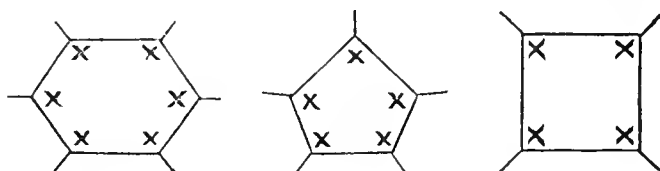
This passage serves to show that Professor Sylvester has a much clearer idea of the scope and real meaning of the so-called structural formulas, or, as he well calls them, "chemico-graphs," than many chemists have. The words: "The question is one purely of colligation or linkage in the abstract," should be used with emphasis whenever the dangerous task is undertaken of explaining to beginners the meaning and use of the formulas. Misapprehension in regard

to this point is really the cause of most of the objection that is raised to structural formulas by persons who have not very thoroughly familiarized themselves with the process of evolution which has led very naturally to the conceptions at present held by the leading chemists of the world. Indeed some of the most telling objections raised have been based in a vague sort of way upon the idea that the formulas did violence to certain (undefined) mathematical truths. It is, hence, doubly interesting to find a mathematician using the language which we have above quoted.

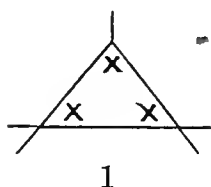
In another passage the same idea is expressed in a different way: "Chemical graphs, at all events for the present, are to be regarded as mere translations into geometrical forms of trains of priorities and sequences having their proper *habitat* in the sphere of order and existing quite outside the world of space."

The conception of variable valence which causes so much difficulty for chemists finds no analogy in algebra, but Prof. Sylvester recognizes this difficulty, and proposes an hypothesis for the purpose of explaining the variability. This hypothesis is certainly much more satisfactory than any that has thus far been proposed; though it is well to bear in mind that those hitherto proposed scarcely deserve the name of hypothesis. "It is this: leaving undisturbed the univalent atoms, let every other  $n$ -valent atom be regarded as constituted of an  $n$ -ad of *trivalent atomicules* arranged along the apices of a polygon of  $n$  sides. Thus sextivalent, quinquivalent and quadrivalent atoms in

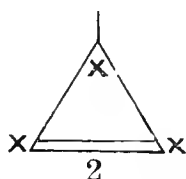
their maximum valence will be represented by the adjoining figures where the letters denote *trivalent atomicules*.



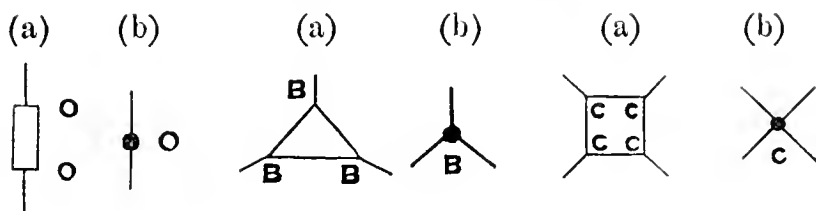
When the valence is reduced by two we need only conceive any one of the side loops doubled or a new loop as formed by the coalescence of a pair of free bonds or tails. . . . We have thus a conceivable and conformable-to-analogy method of accounting for the variability in question. So likewise, a trivalent atom with maximum state of valence will be represented by figure 1



and when univalent by figure 2. This hypothesis of atomicules, if unobjectionable on other grounds, would not be open to the charge of having any tendency to disturb or complicate the existing graphology; for we should still be at



perfect liberty to substitute for the graphs (a) of the subjoined figures the abridged notation (b), and should naturally



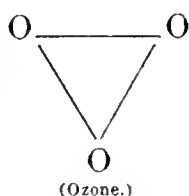
do so when considering the relations of atoms to each other. The beautiful theory of atomicity has its home in the attractive, but somewhat misty, borderland lying between fancy and reality, and cannot, I think, suffer from any not absolutely irrational guess which may assist the chemical enquirer to rise to a higher level of contemplation of the possibilities of his subject."

In a letter to Prof. Sylvester, by Dr. Frankland, published in the *Amer. Journ. Mathematics*, Vol. I. p. 345, reference is made to the hypothesis just described in the following words: "It seems to me that your conception of the constitution of atoms may prove of great value, not in its application to variation of atomicity, but in furnishing an explanation of the behavior of certain atoms which has long puzzled me and doubtless also other chemists. Carbon affords the best example of what I mean. The strong affinity of carbon for carbon is a quality upon which depends the very existence of nearly every organic compound, and sharply distinguishes these compounds from the almost equally complex siliceous minerals, in which the atoms of silicon are, in no single instance, combined with each other. The most obvious explanation would be that the bonds of carbon are  $+$  and  $-$  to each other, whilst those of silicon are identical or endowed with energy of the same kind and intensity. But it is a remarkable fact that hitherto, with very few and dubious exceptions, all attempts to establish a difference between the four bonds of the carbon atom have failed. Thus, if an atom of carbon be combined with four atoms or monad groups, a, b, c, d, of which a and b are  $+$  and c and d  $-$ , it does not matter apparently in what order these bodies are introduced to the carbon atom; for instance, if the body  $+$ a be replaced by a negative body  $-$ c, and  $+$ f; and if then in another molecule of  $-$ c be replaced by  $-$ c and  $+$ a by  $+$ f, the two new molecules are identical and not isomeric as might be expected. But if, according to your conception, each bond is tripartite, it could, of course, exert either  $+$  or  $-$  energy according to the quality of the atom or group presented to it."

We must confess that to us there is something very attractive in this hypothesis of "atomicules." Not that it gives a full and satisfactory explanation of the numerous puzzling

facts known to chemists, which have always interfered with the acceptance of the idea of valence; but it approaches more nearly to a working hypothesis than any idea that has as yet been proposed. It seems possible that experimental methods now in use may, if properly applied, enable us to test the accuracy of the hypothesis.

Some such possibility is suggested by the remarks\* of Prof. Mallet on the paper under consideration. In these remarks, attention is called to the fact that the conversion of ozone into ordinary oxygen is accompanied by an evolution of heat. The ordinary graphs for oxygen and ozone do not offer any explanation of this fact, for the number of bonds for each atom and the average distance between it and the other atoms with which it is connected is just the same in  $O=O$  and in



On the other hand, by means of the graphs of Professor Sylvester, a possible reason for the observed thermal relations can be discovered. For "the average distance between the atoms, as also between the atomicules, is increased in passing from the ordinary form of oxygen to ozone; or, in other words, the production of ozone from oxygen gas is an act of *partial* chemical decomposition,† not resulting in the detachment of the constituent atoms from each other; on the contrary, leaving them in a state of definite chemical combination, but removed further apart than they were in the more stable form of the element; hence, as in complete, so in this which I have called partial decomposition, extraneous energy is necessary; while the reverse change, from ozone back to ordinary oxygen, is an act of more intimate chemical union, resulting in closer approximation of the constituent parts of the molecule, and hence attended with evolution of energy, as in the form of heat."

Similar observations in connection with the allotropic forms of phosphorus, and possibly also with the different varieties of sulphur, might throw some light, though it would be but faint, upon the hypothesis of "atomicules." It is not probable, however, that any very satisfactory experimental evidence, either for or against the existence of atomicules, can be given. Whether, after almost infinitely more is known than is at present known, in regard to the conduct of substances towards one another under the most varied circumstances, it will be possible by mathematical reasoning to pierce the veil which now hides from us the structure of matter, is a question which cannot be positively answered. But the attempt to answer it will necessarily reveal to us very clearly our present position.

EDITOR.

\*Amer. Journal Mathematics, Vol. I. p. 277.

† The word *deformation* has been suggested to us to express this idea.—ED.

LECTURE NOTES ON CHEMICAL PHYSIOLOGY AND PATHOLOGY. By Victor C. Vaughan, M. D., Ph. D. Pp. 315. Ann Arbor Printing and Publishing Company.

This book is an unusually good one of its kind. Of course a treatise on physiological chemistry which almost entirely avoids the consideration of the chemical processes going on in the living body (containing, for instance, hardly any reference to such important questions as the sources of animal fats and of glycogen), is very incomplete. But we imagine that practically no one will be deceived by the title. It has somehow come to pass that the study of the proximate and ultimate constituents of the dead body, the composition of the secretions of the living body, and some account of the chemistry of digestion, are considered the end and aim of physiological chemistry, and on such points the information given by the author is tolerably full and more accurate than common. The selection of topics has no doubt been largely influenced by their fitness for practical study in the laboratory and to a certain extent by their importance to the medical practitioner: thus more than half the book is devoted to the consideration of the urine. But on any principle of selection we find it hard to account for the absence of even a brief account of the gaseous interchanges occurring in respiration; since in the hands of Pettenkofer and Voit and others they have thrown more light than any other material exchanges between the living animal and its environment, upon the chemical processes in the body in rest or work and on different diets. At least rough quantitative examination of the inspired and expired air could be carried on by most students; and we think the more advanced might well be taught something of the mode of examining the blood gases.

The great bulk of the work is of course a compilation, but in several subjects the author records experiments made on himself or on his students with their co-operation. Those on the relationship of the daily urea excretion to the kind of food eaten and to muscular work, although they give no new results, are especially welcome now, when under the powerful influence of Flint there seems some danger in this country of a revival of Liebig's erroneous views. The concise critical statement of the question given by the author will also be useful, and under present circumstances we would have been glad to see it expanded.

Of errors we have detected but few. One is the statement that Kühne has proposed the terms antipeptone and hemipeptone as equivalent to the parapeptone and peptone of Meissner. In fact Kühne strives to show that parapeptone is not a product of normal digestion at all, but that under the influence of the gastric secretion two groups, which he calls the *anti* and *hemi* groups, are produced by the splitting up,

with hydration probably, of albuminous bodies, which latter he considers to contain anti- and *hemi*- residues. If this view be correct, it is of such importance as giving the first clue to the constitution of this class of bodies, that we think some space might well have been devoted to an account of it.

It will, however, be so much of a novelty to have a physiological chemistry of manageable size and general accuracy, to place in the hands of students as a guide in their laboratory work, that we have no doubt Dr. Vaughan's book, in spite of its faults, (which are nearly all of the easily condonable type of sins of omission) will be welcome wherever there is a physiological laboratory.

H. NEWELL MARTIN.

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BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS. By J. W. Mallet.

A thoughtful survey of the varying uses made by man of the forms of matter which surround him, and of the different methods by which he works these materials and fits them to his service, is always interesting. The ample and valuable reports upon the progress of industrial chemistry which appear nowadays at frequent intervals are not simply useful to the manufacturer engaged in each special branch of industry, but may be read with pleasure and profit by the student of scientific chemistry, who can look beyond the mere results of experience and trace the history of principles side by side with that of their application; and by the well educated general reader, who may see spread before him one field, and that not a small one, of our expanding domain over external nature, the domain which constitutes our material civilization.

The very thoroughness, however, with which the best reports of this kind are prepared makes it somewhat difficult to obtain from them a broad, general picture of the condition of chemical industry from time to time. One's attention is taken up and one's memory wearied by the multitude of details, a large proportion of which are of subordinate or temporary importance, while the transition from one great phase of a manufacture to another is thus rendered less noticeable; just as, when one becomes entangled in the movement of a great army, the impression of endlessly succeeding men and horses and individual commands makes it far from easy to obtain any general idea of the main direction taken or the changes in the positions taken up. It may, therefore, be worth while to attempt a short, condensed sketch of the principal changes which the last few years have brought about in the condition of the manufactures most

dependent upon chemistry, overlooking the slow and often uncertain steps by which results have been reached, and the smaller details of improvement in the results themselves. Such a sketch must of necessity include matters for the most part familiar to all those whose attention has been given to this class of subjects, but need not on that account be without interest even for such.

It is not easy, nor is it necessary, to define with exactness what is meant by thus speaking of the "last few years." Different industries do not advance *pari passu*, and the position in which one is found at present may be essentially that which it assumed twenty or twenty-five years ago, while another may have undergone an important change within two or three or ten years, and a third may be now in the very act of transformation. It best answers the purpose aimed at to note for each the chief features of its present condition and most recent changes of importance. In some directions little or nothing is to be observed of really noteworthy progress, the history of a manufacture for a long time past involving either merely improvements in small though perhaps useful details, or attempts at new processes tried for a while and then allowed to pass out of use as unfit to replace older methods.

In such a general survey as is proposed, the salient points most attracting attention may be classified somewhat as follows:

I.—Improvements in the attainment of old results; depending on:

1. New sources of supply of long known materials.
2. Introduction of new materials.
3. New processes involving either new principles or modifications in the application of old ones.
4. New mechanical appliances.

II.—Attainment of new results arising from:

1. New means of production.
2. New demands from consumers.

III.—Disposition made of:

1. Old and
2. New secondary products or waste materials.

IV.—New and special conditions of work, as:

1. Changes in labor market.
2. Changes in legislation, taxation, tariffs, &c.
3. Exceptional demands for particular products, as under stress of war, blockade, &c.

V.—Problems:

1. Long outstanding.
2. Recently suggesting themselves, which still await solution.

As regards the several departments of industry which may

be claimed as chemical, or closely related to chemistry, they will be run over pretty nearly in the order in which the writer has been in the habit of discussing them in annual lectures to one of his classes of students.

*Fuel, and Arrangements for the artificial Production of Heat.*

Under this head we may fairly place foremost in importance among still recent improvements the admirable gas furnace of Siemens. The invention, in its practical shape, involves two distinct ideas. First, the production by simple, readily controlled means, and from cheap, even refuse forms of combustible matter of a purely gaseous fuel, the supply of which to the furnace can be regulated as easily as by turning a stop-cock, while all injury to the material heated arising from soot, ashes and unburnt particles of solid fuel is completely obviated; secondly, the arrangement of a hearth in which this gas may be burned in admixture with air after both have been separately raised to a high temperature by passage through heated chambers filled with loosely piled fire-brick, while the heating of a second pair of such chambers, through which the gas and air may be turned after the others have cooled down, is accomplished by leading through them on the way to the chimney the products of combustion from the other end of the hearth. By shifting the dampers or valves at intervals the air and gas supply is transferred from one end of the hearth to the other, one pair of fire-brick chambers being always engaged in storing up heat which otherwise would go to waste with the draft up the chimney, while from the other pair such accumulated heat is taken up by the gaseous fuel and air on their way to the hearth. In fact we have here essentially the principles of the "oxyhydrogen blow-pipe" and the "hot blast" combined and applied in simple form and upon a grand scale. As to the temperature so producible, it may be said that its practical limit is found in the difficulty of getting material infusible enough for the hearth lining, while the actual temperature at which the furnace is worked may be regulated by simply turning on or off the valves which control the admission of gas and air, and with a precision far beyond that which depends upon any mechanical stoking of solid fuel. And, most difficult object of all to attain with any of the older forms of furnace, and of great importance often from the chemical point of view—the *relative* supplies of combustible gas and air may be easily so adjusted by using the respective valves independently as to yield in the hearth an oxidizing, a reducing, or a perfectly neutral atmosphere.

Whether in connection with the "regenerator" gas furnace or the old-fashioned reverberatory, a most useful labor-saving

appliance of comparatively recent years is the rotating hearth, a cylindrical or barrel-shaped vessel of iron lined with infusible material which is slowly revolved about its axis of figure by gearing on the outside, while through it from end to end passes the flame on its way to the chimney; the material to be heated being turned over and over, its different parts mixed, and fresh surfaces exposed to the flame, without the necessity for severe manual labor on the part of workmen with iron bars, and without the exposure to air which the introduction of these bars entails.

The simplicity and economy with which combustible material, otherwise of small value, may be converted into gaseous fuel in the "generator" of Siemens' invention, and the advantages which attend the use of fuel in this form, apart from its employment in his furnaces, suggest a probably much wider field for its use in the future in connection with various branches of chemical manufacture. "Water-gas," essentially a mixture in various proportions of hydrogen, carbon monoxide, carbon dioxide, and atmospheric nitrogen, obtained by bringing water in contact with glowing carbon, whose combustion is properly regulated, seems to have first been distinctly noticed by Fontana in 1780, and has repeatedly since then attracted attention, but no arrangement for its ready production at will has combined so many practical advantages as the Siemens generator.

To some extent the immense natural supplies of combustible gas—chiefly methane and ethane—obtainable in portions of the petroleum region of Pennsylvania, Ohio and West Virginia, have been utilized as fuel, but the merely local character of such supply must always very much limit its importance.

The great loss of heat, amounting to about two-thirds of that producible from the fuel used, which is involved in allowing the formation in a furnace of carbon monoxide, and its escape unburnt or burned only to waste,\* has come to be pretty generally understood; and especially from blast furnaces used in making pig-iron, is this gas now very commonly collected by means of suitable flues from the upper part of the furnace, and made use of not only for purposes connected with the working of the furnace itself, as raising steam for the engine and heating the blast, but occasionally as the means of producing heat for other objects, as burning lime, bricks, common pottery, &c. The time is not far back when this portion of the fuel was almost always wasted.

For certain purposes, though not most prominently for chemical manufactures, the use of *liquid* fuel claims serious attention; but the most valuable material of this kind which

*C	burned to CO <sub>2</sub>	evolves	96.960	heat units	(obtained by complete combustion).
CO	"	"	CO <sub>2</sub>	"	67.284 " " (lost by escape of CO).
C	escaping as CO	"	29.676	"	"

we possess, crude petroleum, distinguished by its great heat-producing power, its abundance and cheapness, still awaits a satisfactory solution of the problem of its application.

When lower temperatures than those directly resulting from combustion are required, steam becomes invaluable as the means of transmitting, distributing and regulating the supply of heat, and both at the boiling point and superheated, both at ordinary and high pressure, it plays a more and more important part in the arrangement of chemical factories, the water resulting from its condensation being at pleasure allowed to mingle with or excluded from the material heated, while the escape of steam itself is sometimes available as the means of producing mechanical agitation.

It may not be unworthy of mention that the "slag-wool" now produced upon a fairly large scale by blowing a jet of steam or air forcibly over the surface of furnace slag in a state of fusion, affords an excellent material for jacketting boilers, steam-pipes, hot-air flues, &c., in order to greatly diminish, by its low conducting power, the loss of heat in transmission, while danger from fire and annoyance from rotting or mouldering of organic substances, are obviated by the unalterable character of this mineral material.

### *Metallurgy — Iron.*

The grand fact in the history of iron for the last twenty years has been the gradual but pretty rapid substitution of the softer varieties of steel to a very large extent for wrought iron. The earlier experiments of Bessemer and some others who worked at about the same time, were directed to the production of this latter material by a quicker and easier process than "puddling" for the removal of the carbon of cast-iron. These experiments were unsuccessful so far as the complete removal of carbon and production of thoroughly soft, pure iron was concerned; but they proved the feasibility of manufacturing steel directly from cast-iron with far less expenditure of time, fuel and labor than older methods, such as "cementation," involved, in which carbon had first to be removed, producing wrought iron, and subsequently added again slowly and in restricted amount. The new processes, moreover, carried with them the great advantage of operation at so high a temperature that the metal was completely fused, and hence much more uniform in character than when masses were consolidated by welding only from parts varying in the amount of carbon, and hence in physical properties, and retaining also in the case of bar-iron more or less remains of slag. It did not take long to show that these characteristically new processes were not destined to replace the older ones for the manufacture of wrought iron, properly so-called,

but it was not so quickly perceived that neither were they fitted for the production of the best steel, of such kinds as the name had previously been most connected with, and for such uses as it had previously been most largely applied to. Gradually it became apparent that the true function of the newly invented methods was mainly the production of a new material, containing carbon in relatively small amount, combining the toughness and workable qualities of wrought iron with the great tensile strength, rigidity, some of the hardness, and especially the homogeneity due to practicable fusibility, of steel. The "mild steel" which is the essential result of the recent processes of manufacture, is not the "tool steel" which not many years ago was pictured in every one's mind in connection with the name steel, but it is a substance available for a far wider range of uses and applicable upon a far greater scale.

Of the various individual processes which have been proposed and tried for the rapid production of mild steel, decidedly the most successful have been those of Bessemer and Siemens; the former consisting essentially in forcing a blast of air under high pressure into molten cast-iron in a suitable "converting vessel," thus rapidly burning out the carbon and silicon, mixing with the fluid metal a determined amount of separately fused cast-iron containing a known amount of carbon, and casting the product into ingot moulds; while the latter brings into play the admirable peculiarities of the gas furnace, by fusing together at the extremely high temperature which it affords, and in the entirely controllable chemical atmosphere of its hearth, pig-iron and scrap wrought-iron, as suggested by Martin, or pig-iron and iron ore (an oxide) on the plan of Uchatius, but on a much greater scale in either case, so apportioning the carbon and iron left together in the fused product that steel of the required character shall be obtained. In a sense it may be said that the invention of Siemens, leading to the manufacture of "Siemens-Martin" and "Landon-Siemens" steel, has supplemented the Bessemer converter, and by providing a way for profitably using up vast stores of old wrought-iron already on hand, has permitted the more rapid substitution of steel manufactured by both methods. By these two processes, within the last two or three years an annual product of more than 2,500,000 tons for the world at large has been turned out.

During the period in which so much attention has been concentrated upon steel, much has been learned in reference to the effect in its production and upon its properties of even very small quantities of other elements than iron, though much still remains to be ascertained in this direction.\* The

\*An important paper by V. Deshayes has recently been published (Bull. de la Soc. Chim. de Paris—20 Fév. & 5 Mars, 1879), giving the results of an extensive examination of the influence upon the physical properties of steel of its various minor constituents—phosphorus, silicon, manganese, &c.

most important points which have been ascertained are those in regard to the benefit derivable in the manufacture, particularly of Bessemer steel, from the presence in the iron of manganese and silicon; the chief function of the former being the removal, to some extent, of sulphur, phosphorus and oxygen, which, if allowed to remain, greatly impair the mechanical excellence of the product, while they exhibit a stronger tendency to combine with manganese than with iron, and thus get carried off into the slag; silicon, on the other hand, aiding by its combustion to keep up the high temperature in the converter which maintains the fluidity of the metal, and uniting when burned with the basic oxides to form and separate from the metal a removable form of fluid slag. The observed benefit arising from the presence of these two substances has stimulated the production, for use in connection with steel-making, of cast-iron rich in silicon, of crystalline "spiegel-eisen," containing a large and uniform amount of carbon along with manganese, and lately of alloys of iron and manganese—the so-called ferro-manganese—containing, as in the product of the French Terre-Noire works, up to 65, and even 85, per cent. of the latter metal. Another point, and of unexpected character, has but lately been ascertained—namely, that if the percentage of carbon in steel be reduced, phosphorus may be admitted to an extent which would be seriously injurious if the normal amount of carbon for the kind of steel required had been present. Some remarkable specimens of steel from works on the Siemens-Martin plan, in New Jersey, in the possession of the writer, illustrate this distinctly. Notwithstanding the numerous attempts, too often reported on by interested parties, to produce valuable alloyed forms of iron or steel by addition of other metals, most of which attempts have led to no permanent results of real importance, it remains much to be desired that a systematic examination should be made by impartial hands of the alloys of iron, with and without the presence of carbon, trustworthy analyses being made of the products, and at the same time their physical characters submitted to well-defined tests. Up to this time the only two of the more refractory metals which seem to have proved themselves capable of influencing in any useful way the properties of steel are tungsten and chromium, which give hardness, accompanied however by increased brittleness. The increase of retentive capacity for magnetism which tungsten is reported as producing may perhaps prove valuable in the construction of dynamo-electric machines.

As regards wrought-iron, whose day for many purposes can by no means be considered as gone by, the most notable manufacturing improvement has undoubtedly been the introduction of mechanical puddling as a substitute for the more laborious and less uniform hand-work. After many previous

attempts, success in this direction has come with the application of the rotating hearth, of which the Danks furnace arrangement deserves to be taken as the type. The more general use of currents of water through double furnace-walls as the means of allowing the highest temperatures within, with diminished risk of injury to the walls themselves, is an extension of the long-used water-backs of the refinery furnace.

For cast-iron, aside from the marked increase in the size of many of the furnaces built, and in some hands the use of a blast of considerably higher temperature than was usual a few years ago, the question of most interest has been that of the elimination from the metal of phosphorus and sulphur, particularly the former, with a view to the supply of metal to the steel-makers suited in this respect to their requirements, since the modern methods of steel manufacture do not tend to remove phosphorus if present, the Bessemer process even relatively increasing its amount, and its retention in the steel to any large extent being ordinarily in the highest degree objectionable. The comparative scarcity and therefore cost of ores originally free, or nearly so, from phosphorus, while others are abundant against which the presence of this element can alone be urged in objection, renders the problem one of great importance.\* Of the many plans proposed for getting rid of the undesirable element, two seem most to deserve notice. It has been found that in Cleveland ironstone from Yorkshire in England, and the same is probably true of many other ores, the phosphorus exists mainly, if not solely, as calcium phosphate, and that by washing the ore with a solution of sulphurous acid, obtained by passing the sulphur dioxide from burning pyrites into water, a large proportion, up to even 90 per cent. of the phosphorus, may be dissolved out and removed. It has been urged against this process as a fatal objection that the ore must be in fine powder to allow sufficiently thorough contact with the liquid acid, while the pulverulent condition unfits it for smelting in the ordinary way. While this is true as regards after use in the blast furnace, it seems quite possible that ore in powder might be managed in the Siemens furnace for the production of "Landon" steel, and, in the absence of material naturally pure enough, this process of preparatory washing may yet find application to a certain extent. The other plan to be mentioned has more extensive claims to attention, if the facts upon which it rests are fully confirmed by further experience, and if it can be brought into practically workable shape. Mr. Lowthian Bell, to whose intelligently

\* It seems possible that one of the main features of Heaton's process for making steel from cast-iron rich in phosphorus—viz. oxidation by sodium nitrate at the bottom of a converting vessel—may be revived in perhaps a more permanently successful form. M. Gruner asserts of late (*Bull. de la Soc. d'Encourag. pour l'Indust. Nation.* Jan. 1879) that phosphorus may be removed in either the Bessemer converter or the Siemens furnace if a refractory *basic* lining be substituted for one of siliceous material.

directed researches we owe much important information in regard to the chemistry of iron-smelting, believes he has ascertained that phosphorus may be in large measure removed from melted cast-iron by oxidation at a temperature lower than that suited for puddling, the oxygen being derived from a bath of molten oxide of iron or slag very rich in such oxide; though at a higher temperature, at all approaching that of the Bessemer converter, phosphorus would be taken up again by the iron from the very same slag. It is proposed that the iron shall be brought rapidly into contact with the rich slag by running it from the furnace into a circular converting vessel, revolving about its axis and containing the slag already in a state of fusion. In one experiment it was found that the phosphorus in iron from Cleveland ore could by such treatment be brought down to .055 per cent., while continued contact, at full puddling heat, with the puddling furnace slag which had served as the means of purification, raised the proportion of phosphorus again to .153 per cent. in 65 minutes, and to .365 per cent. in three hours. These experiments are suggestive and full of promise that a solution of this important problem will yet be found, though as yet it cannot be said to have been reached in a practically useful and generally applicable form.

In noting the chemical aspects of the iron and steel industry, as developed in the last quarter of a century, we can not overlook the magnificent scale upon which the mechanical appliances used in working the metal have outgrown their former dimensions.

A visit to such works as those of Creuzot in France, Krupp's establishment at Essen, in Germany, the heavy gun factories at Chatham and the armor-plate mills at Sheffield, in England, or even to several of the works which have grown up in this country, presents a truly impressive picture of mechanical power directed and controlled by human brains. Such a single tool as the great Creuzot steam-hammer, with its 75 or 80 tons of iron falling 18 feet upon an anvil of nearly 900 tons, and capable of forging masses of steel of 120 tons or more, represents a marvellous advance upon the means at the command of the iron-workers of fifty or even twenty years ago. Yet the very source of the demand for these mighty machine-tools, the growth of the manufacture of iron, and yet more steel, has in the improved character of the material produced opened up a still wider field and enlarged possibilities for the employment of mechanical energy upon the grandest scale.

*(To be continued.)*

## NOTES.

### *Material for Standard Weights and Measures.*

FRIED. MOHR suggests that a block of uncrystalline, black marble be used for the standard meter. The block should have the dimensions: 111 cm. in length; 20 cm. in height and breadth; *i. e.* it should be a parallelepipedon of 44,000 cc. The specific gravity being 2.7, the weight of the block would be 118.8 kilograms, or nearly  $3\frac{1}{2}$  cwt. These dimensions afford sufficient protection against, 1, breaking; 2, distortion; 3, sudden action of heat; 4, theft; and further they admit of the possibility of determining the temperature of the block exactly, as a thermometer can be sunk into a hole reaching to the middle of the block. The coefficient of expansion of black marble is 0.0000045 for  $1^{\circ}$  C. As the meter has 1000 mm.,  $\frac{1}{1000}$  mm. = 1 millionth part of a meter. 4.5 thousandths of a millimeter =  $\frac{1}{222}$  mm., a distance which cannot be seen without the microscope.

The author considers rock-crystal the best material for weights, but as such weights would necessarily be very dear, he suggests the use of solid glass containing a large proportion of silicic acid. The conditions to be satisfied are: 1st. That all the weights should be made from materials of the same density; 2d. That the specific gravity of the pieces used should approach nearly to that of the substances commonly weighed; and 3d. That the weights should have a certain hardness to protect them from wear.—(*Annalen der Chemie*, 194, 1.)

### *Nitrous Oxide as an Anæsthetic Agent.*

P. BERT has made some experiments on animals which indicate the possibility of employing nitrous oxide as an anæsthetic agent in the cases of operations requiring considerable time. The use of the gas is dangerous because it must be inhaled in pure condition, and hence suffocation soon follows in consequence of a lack of oxygen. The fact that the gas must be inhaled in pure condition signifies simply that its tension must be equal to one atmosphere in order that enough shall enter into the system. If, however, the patient is placed in an apparatus in which the pressure is increased to two atmospheres, then a mixture of 50 per cent. nitrous oxide and 50 per cent. air may be employed. The anæsthesia will be effected, while at the same time the normal quantity of oxygen

finds its way into the blood, and normal conditions of respiration are preserved. The author's experiments on animals showed the correctness of the above reasoning. Unconsciousness was reached while normal respiration continued, and this condition could be maintained for an hour. On removing the bag which contained the mixture of gases the animal returned to its normal condition after two or three inhalations of fresh air. During the action of the anæsthetic, the animal showed no signs of pain even when nerves laid bare for the purpose were subjected to pressure or when its limbs were amputated. No bad after-effects were observed.—(*Comptes rendus*, 87, 728.)

### *Purification of Mercury.*

J. W. BRUEHL recommends the use of chromic acid for the purification of mercury. Twenty-five kilograms of mercury which contained a considerable quantity of Wood's metal were perfectly freed from the foreign substance in about two hours. To 1 liter water are added 5 gr. potassium bichromate and a few cubic centimetres sulphuric acid, and an equal volume of mercury is well shaken with this mixture. The metal breaks up into globules, while a very small quantity is transformed temporarily into red chromate. The flask is shaken until the red powder has disappeared, and the aqueous solution becomes pure green from the chromium sulphate formed. A strong current of water is now passed into the flask, and a fine gray powder which lies upon the surface of the mercury and between the globules, and consists of the oxides of the metals, is thus washed away. According to the degree of impurity this process is repeated once or twice more, and finally the whole is shaken with distilled water until no more gray powder is washed away, and the water remains perfectly clear.

This method was tested with a large quantity of waste mercury that had accumulated in the author's laboratory in consequence of the amalgamation of the zinc plates of a battery. Much of this mercury contained so much zinc, copper and lead that it was solid. In the course of an afternoon it was purified so completely that when shaken in a porcelain dish it did not leave a trace of a mark upon the porcelain.—(*Ber. deutsch. chem. Gesell.* XII. 205.)

### *On the Preparation of Hydrogen Sulphide in Chemico-Legal Examinations.*

Formerly hydrogen sulphide for chemico-legal examinations was unhesitatingly prepared from crude materials, generally from commercial iron sulphide with crude sulphuric or hydrochloric acid, probably because it was thought that the formation of arsine in a liquid in which hydrogen sul-

phide is being evolved was impossible. In 1869 J. Otto found that arsine was contained in hydrogen sulphide from impure materials. Myers found later that arsine and hydrogen sulphide can exist in each other's presence at ordinary temperatures. Myers is of the opinion that the formation of arsine is due to the presence of arsenic in the acids and not in the iron sulphide. The author states that his own experiments serve in general to confirm the opinion of Myers, but he adds that the iron sulphide may also play a role in the formation of arsine.

Whatever the origin of the arsine may be, it is plain that hydrogen sulphide containing this impurity is not fit for use. *It is hence absolutely necessary to make the hydrogen sulphide used in forensic examinations from pure materials, free from arsenic.* Dragendorff recommends that the iron sulphide employed be made from washed flowers of sulphur and pure wrought iron, and that the first part of the distillate obtained in rectifying sulphuric acid be used for decomposing the sulphide. R. Otto recommends the use of calcium sulphide, which can be easily prepared by igniting gypsum with charcoal, and this he decomposes with pure hydrochloric acid. If the acid is allowed to drop slowly upon the calcium sulphide under water, the sulphide being broken up in coarse pieces, a quiet and regular current of pure hydrogen sulphide is obtained.—(*Ber. deutsch. ch. Gesell.* XII. 215.)

#### Notes on "Uranine."

The substance to which the trade name "Uranine" has been given is now to be found in the hands of dealers in coal tar dye-stuffs, and has of late been made the subject of various newspaper notices, drawing attention, sometimes in rather a fanciful way, to the remarkable fluorescence of its solution. The material appears as a red powder of somewhat the tint of cuprous oxide, directly soluble in water, the solution having an orange color by transmitted light, exhibiting vivid green fluorescence, and directly dyeing animal fabrics a bright golden yellow.

1. Qualitative examination shows that this coloring material is sodium-fluoresceine, readily developing by bromination the beautiful aurora red tints of eosine. Traces of the potassium and calcium compounds are also detectable by means of the spectroscope, but they are accidentally present only.

2. When the substance in the dry state is heated over a lamp flame, it undergoes partial fusion and rapid charring, producing a very voluminous coal, from the interior of which the fused and decomposing mass is rapidly pushed out in oddly contorted, worm-like cylinders, reproducing the appearance of the "Pharaoh's serpents" (of sulpho-cyanate of mercury) which were sold as toys a few years ago. This effect is most readily

observed with a little of the powder taken up on a loop at the end of a small platinum wire.

3. The fluorescence, which persists in extraordinarily dilute solutions, is not observable in those of more than a certain degree of concentration. In order to determine approximately what degree of dilution is needed to produce the phenomenon, 1 gm. of the powder was dissolved in 10 cc. of water at 15° C., and more water gradually added. With 40 cc. fluorescence began to be faintly seen; the effect was not well marked until about 100 cc. had been used, and it became notably more brilliant up to a dilution of about 1 : 2000.

This effect of dilution is suggestive of partial dissociation of the alkaline compound under the influence of the "mass" of the water, for on preparing a cold solution of a strength just too great to show fluorescence and applying heat, the green light became perceptible, while heating to an equal extent did not develop fluorescence if a lump of solid sodium hydrate had previously been dropped in and dissolved.

4. "Uranine" may be used as a distinctive test for bromine, the change from yellow to eosine-red being well marked, and the reaction producible with a small enough quantity to give it practical value. Thus, on dyeing a bit of white silk with a solution of 1 gm. uranine in 100 cc. of water and letting the fabric dry, .0005 gm. of bromine in (saturated) bromine water directly applied produced a minute rose-colored spot; .005 gm. of potassium bromide, representing .0033 gm. bromine, was placed in a very small test-tube with a few milligrammes each of manganese dioxide and sulphuric acid; a bit of white silk, 20 mm. by 4 mm., having a spot of 5 mm. by 2½ mm. dyed yellow with uranine, dried, and one half the surface of the spot slightly remoistened, was placed in the upper part of the tube, and the bottom was gently warmed, a fairly recognizable change from yellow to red of the moistened surface was produced. The change of color is not brought about by chlorine, iodine, or the lower oxides of nitrogen. Much chlorine along with bromine bleaches the fabric, but even then careful observation during the progress of the action will show the rosy tint around the edges of the spot which has been dyed.

*Univ. of Va., Feb. 24, 1879.*

J. W. MALLETT.

*The Amalgams of Chromium, Manganese, Iron, Cobalt and Nickel,  
and a new Process for the Preparation of  
Metallic Chromium.*

H. MOISSAU states that when a concentrated solution of protochloride of chromium is shaken with sodium-amalgam, part of the latter decomposes water, and oxide of chromium is precipitated. Another part produces, by double decomposition, chloride of sodium and an amalgam of chromium. This freed

from sodium by boiling water is less liquid than mercury, becomes covered with a black layer of oxide on exposure to air, and is slowly decomposed in presence of dry air, more quickly in presence of water. Heated in hydrogen to  $350^{\circ}$  it leaves a residue of metallic chromium in the form of black, amorphous powder, which becomes suddenly incandescent when heated to red heat on platinum foil, and is converted into the green sesquioxide. The metallic chromium thus obtained is not attacked by boiling sulphuric acid nor by nitric acid, and only slowly by hot hydrochloric acid. This method of obtaining the amalgam is applicable to manganese, iron, cobalt and nickel. Schoenbein obtained in this way amalgams of iron and manganese, and Damour those of nickel and cobalt, by zinc amalgam. The author also obtained an amalgam of manganese by electrolysis of the protochloride, using a negative electrode of mercury. He was able in this way to obtain a crystallized product, which when distilled at  $440^{\circ}$  left manganese in the form of powder. This when touched with a drop of strong nitric acid became incandescent. It also decomposes water slowly at ordinary temperatures, more rapidly at  $100^{\circ}$ . Electrolysis also gave amalgams of nickel and cobalt, which were quite quickly oxidized by contact with water. The amalgams thus obtained were less rich than those of sodium, which fact the author attributes to opposing currents produced by the action of the amalgam upon the liquids in contact with it.—(*Comptes rendus*, 88, 180.)

#### *Lead in Crystals of Potassium Iodide.*

E. SCHERING calls attention to the fact that concentrated solutions of potassium iodide take up lead iodide. This is of special importance, inasmuch as the iodine employed in the manufacture of potassium iodide sometimes contains lead. In concentrated solutions of potassium iodide which contain lead, hydrogen sulphide at first causes a precipitate, but all the lead cannot be precipitated by this means; for the clear filtrate when further evaporated yields crystals containing lead. In order to remove all the lead from the potassium iodide it is necessary to dilute the solution greatly, and then precipitate by means of hydrogen sulphide.—(*Ber. deutsch. chem. Gesell.* XII. 156.)

#### *Photographic Observations of the Spectrum of Oxygen.*

HERMANN W. VOGEL has photographed the spectrum of pure oxygen, using for the purpose the gelatine bromide of silver plates prepared by Wratten and Wainwright in England. These plates, which have only recently been introduced, are *fifteen times* more sensitive than the most sensitive known wet

plates. The photographs will be published in the "Berichte der kgl. Akademie der Wissenschaften in Berlin."

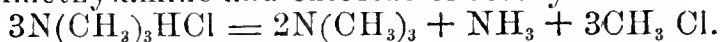
The photograph of the spectrum of *hydrogen* (obtained by electrolysis and by heating potassium formate) has also been taken successfully. In this, not only the three known lines in the blue and violet are shown excellently, but also the red line  $H\alpha$ , coincident with the  $C$  line of the sun, and a number of other lines, of which some belong to mercury, and others still remain to be determined. The author further states, that the fourth hydrogen line (coincident with " $h$ " of the sun) could always be observed by Paalzow and himself with the naked eye, using the simple induction current, notwithstanding the assertion of Lockyer, that this line is visible only at a very high temperature, such as is produced by interposing a Leyden jar.

The photographic observation of the spectra of the most important gases will be continued by the author together with Paalzow.—(*Ber. deutsch. chem. Gesell.* XII. 332.)

#### *A New Chemical Industry established by M. Camille Vincent.*

In countries where sugar is made from the beet the molasses has for a long time been employed to yield alcohol by fermentation. The juice of the beet, as well as that of the sugarcane, contains, in addition to the sugar, a large quantity of extractive and nitrogenous matters, together with considerable quantities of alkaline salts. The waste liquids or spent-wash from the still—called *vinasses* in French—are wastefully and ignorantly thrown away instead of being returned to the land as a fertilizer.

In France where the liquids (*vinasses*) are evaporated to dryness and calcined in order to save the alkaline salts, it is now shown by M. Vincent that the volatile matter given off in the process of calcination may be utilized. Among the products obtained is trimethylamine. When the hydrochloric acid salt of this base is heated to  $260^\circ$  it yields ammonia, free trimethylamine and chloride of methyl:



Large quantities of methyl chloride are thus produced, and this can be used in producing cold, and in preparing certain methylated dyes. Thus a new branch of chemical industry is opened. The subject will be treated more fully in a later number of this journal.—(*Nature*, Vol. 19, p. 308; and *Dingler's polytechn. Journal*, Vol. 230.)

#### *Kolbe's Criticism of Baeyer's Address.*

Last year Baeyer gave an address before the Royal Academy of Sciences at Munich, which Kolbe has recently made the subject of a scathing criticism of a novel character. After a

few introductory remarks of a decidedly uncomplimentary nature, and quite characteristic of the writer, he reprints in his own journal\* Baeyer's address in full in very heavy type, adding here and there a sharp footnote, or an expressive word or two in parenthesis. The address is called a dream because, according to Kolbe, it could not have been the result of thought.

Much of the criticism is expressed by means of interrogation and exclamation points, employed either separately or together; while the words "nonsense," "phrase," "style," "logic," are employed extensively in order to call the reader's attention to the particular kind of error which the writer of the address has committed. We quote some of the longer footnotes in order to give a fairer idea of the criticism. At the beginning of his address Baeyer alludes to Wœhler's discovery of the artificial formation of urea and uses the words, "Considered by itself (it is) only of secondary interest." To this Kolbe remarks: "Wœhler's discovery . . . was considered from the beginning, and is still considered to be one of the most important discoveries which have been made in this century in the department lying between organic and inorganic chemistry, and not only, as Baeyer says, because it formed an epoch in the history of human knowledge, but also because the change which takes place in the transformation of ammonium cyanate into urea by a rearrangement of the atoms in the molecule of the former, *considered by itself* is of the greatest interest even at the present day, when the opinions of chemists in regard to the nature of this change still differ widely." "It is impossible to see what Baeyer had in mind when he wrote the passage and what standard he employs when he characterizes Wœhler's discovery of the artificial formation of urea as one which, considered by itself, is only of secondary importance." Again when Baeyer says, "Wœhler's discovery appearing in the most modest garb," Kolbe remarks: "The modesty of the German chemists in the classical period of chemistry, to-day arrests attention and occasions surprise—a characteristic of the present."

In referring to Baeyer's discussion in regard to the size of molecules and their number in a given space, the critic says: "Nothing is simpler, and at the same time more thankless and worthless, than to make such calculations, in which particularly para-physicists take pleasure. In contradistinction to the real, experimenting physicists, the *ortho-physicists*, who by further experiments test the conclusions which they draw from their experimental investigations, I call those *para-physicists* who by preference use the experimental investigations of others for the purpose of setting up hypotheses, but neglect to test their hypotheses by means of their own, new experiments. It is again particularly the modern chemists who are impressed

\* Journal für prak. Ch. N. F. 18, 432.

by these hypotheses. The third class of physicists, the *metaphysicists*, believe that they can entirely dispense with the experimental foundation in their phantasies in natural philosophy."

The article, with all its curious additions, is certainly interesting and instructive reading.

### *Monument to Liebig.*

The last report of the committee of German chemists on the Liebig monument was given by Hofmann at the last general meeting of the German Chemical Society. A prize was first offered for models, the competition being open to artists of all nations. About twenty models were sent in. These were exhibited in Berlin for three weeks and then sent to Munich, where they were again placed on exhibition. A jury consisting of well-known chemists from different countries, and of artists and other persons of acknowledged critical ability, passed judgment upon the models exhibited, and after considering the matter for two days, awarded the first prize to Professor Mich. Wagnmueller of Munich. The Monument Committee then decided to enter into negotiations with Prof. Wagnmueller, and obtained from him an estimate of the cost of the monument. The estimate was 107,000 marks (\$26,000). It was finally decided by a vote of 3 to 2 to have the statue for Munich made of marble, and that for Giessen of bronze. Professor Hofmann was opposed to the use of marble, and in his remarks before the German Chemical Society he said: "I must confess that my feelings of objection to the erection of a marble statue in Munich are not fully removed; at the same time, the erection of the same statue in marble and in bronze under nearly the same conditions as regards climate, may be regarded as an interesting experiment, the results of which may furnish the chemists of the next century with important points for a decision of the disputed question, *bronze vs. marble*."

### *Death of Heinrich Geissler.*

A loss which all chemists feel is occasioned by the death of Heinrich Geissler of Bonn. In a quiet way this man has done a great deal to advance the physical sciences by devising and perfecting many pieces of glass apparatus in daily use in laboratories. His skill in delicate glass-blowing is too well known to require a word of notice here. His name is perhaps most frequently connected with the so-called Geissler tubes for studying different kinds of electric discharge in rarefied gases or vapors. Besides his well-known mechanical labors, Geissler was engaged in some investigations of a purely scientific character, particularly such as depended for their success upon the construction of peculiarly delicate pieces of apparatus. He died on the 24th of January, at Bonn.

## NEW PUBLICATIONS RELATING TO CHEMISTRY.

## I.—AMERICAN.

- BAYLEY, T. Pocketbook for Chemists, Metallurgists, Dyers, Brewers, etc. New York: Spon. \$2.00.
- ROSCOE, H. E., AND SCHORLEMMER, C. A Treatise on Chemistry. Vol. II. Metals. Part I. 8vo. 504 pp. New York: Appleton. \$3.00.
- WITTHAUS, R. A. Essentials of Chemistry, Inorganic and Organic, for the use of Students in Medicine. 24mo. 257 pp. New York: Wm. Wood & Co. \$1.00.

## II.—ENGLISH.

- BLYTH, A. W. A Manual of Practical Chemistry: the Analysis of Foods and the Detection of Poisons. Illust. 8vo. 484 pp. London: Griffin. 12s. 6d.
- LOCK, A. G. AND C. G. A Practical Treatise on the Manufacture of Sulphuric Acid; with 77 construction plates, drawn to scale, measurements, and other illustrations. Royal. 8vo. London: Low. £2 12s. 6d.
- MUTER, J. Introduction to Analytical Chemistry. 2d Ed. 220 pp. London: Baxter. 7s. 6d.
- PARR, H. Our Domestic Poisons: Dyes and Colors used in Domestic Fabrics. 12mo. London: Ridgway. 1s.
- SMITH, G. Aids to the Study of Practical Chemistry, covering the entire ground required for the honors, science and art paper, and for the B. Sc. examination, London University. 12mo. 160 pp. Stewart. 2s.
- WATTS, H. Dictionary of Chemistry and the allied Branches of other Sciences. 3d Supplement, Part I. 8vo. 840 pp. London: Longmans. £1 16s.

## III.—GERMAN.

- BENTNAGEL, H. Ueber Metabrombenzoesäure, Bromnitro- und Dibrombenzoesäure. Göttingen: Vandenhoeck & Ruprecht. M. 0.80.
- DUFLOS, A. Chemisches Apothekerbuch. 6 Aufl. 2 Lief. Leipzig: Hirt and Sohn. M. 2.00.
- ELLIOTT, J. Ueber einige Derivate d. Styphninsäure u. d. Trinitroorcins. Göttingen: Vandenhoeck and Ruprecht. M. 1.00.
- FELLÖCKER, S. Die chemischen Formeln der Mineralien in geometrischen Figuren dargestellt. Linz: Quirein. M. 3.00.
- GRANDEAU. Handbuch für agriculturchemische Analysen. Mit Vorwort v. Henneberg. Berlin: Wiegand, Hempel and Parey. M. 7.00.
- HASSE, G. Ueber die Einwirkung v. Tetrachlorkohlenstoff auf Phenole in alkalischer Lösung. Göttingen: Vandenhoeck and Ruprecht. M. 1.00.
- JACOBSEN, E. Chemisch-technisches Repertorium. 1877. M. 17.00.
- KOPPE, DR. KARL. Die Messung des Feuchtigkeitsgehaltes der Luft mit besonderer Berücksichtigung des neuen Procenthygrometers mit Justizvorrichtung. Zurich: Schulthess. M. 2.00.

- KRISCHE, C. I. Ueber Nitrobenz- und Nitrotoluide und die Einwirkung v. Wasserstoff auf dieselben. II. Zur Kenntniss der Sulfanilsäure. Göttingen: Vandenhoeck and Ruprecht. M. 1.00.
- LAIBLIN, R. Ueber Nicotin und Nicotinsäure. Göttingen: Vandenhoeck and Ruprecht. M. 2.00.
- LAUBE, G. C. Hilfstafeln zur Bestimmung der Mineralien. 2 Aufl. Prag. Calve'sche Hof u. Univ. Buchh. M. 1.20.
- OSTERMAYER, E. Die organischen Farbstoffe der Steinkohlen-Theer-Industrie. Lörrach: Gutsch. M. 1.50.
- POST, J. Grundriss der chemischen Technologie. 2 Hälfte. Fabrikation der Endproducte. Berlin: Oppenheim. M. 14.00.
- SCHILLING, N. H. Handbuch der Steinkohlengas-Beleuchtung. München: Oldenbourg. 3 Aufl. M. 3.80.
- SCHUNCKE, J. Ueber die Löslichkeit d. Aethyloxydes in Wasser und wässriger Salzsäure. Tübingen: Fues. M. 0.80.
- TOLLENS, B. Einfache Versuche für den Unterricht in der Chemie. Für agricultur-chemische Laboratorien zusammengestellt. Berlin: Wiegand, Hempel and Parey. M. 2.50.

#### UNIVERSITY PUBLICATIONS.—ERLANGEN.

- BINSWANGER. Ein Beitrag zur Kenntniss des Kreosols und einiger Derivate. 21 pp.
- EBERD, R. Ueber die Bestandtheile des Knochenmarkfettes des Ochsen. 20 pp.
- HEINER, G. Ueber die Zusammensetzung des Rindstalg. 20 pp.
- KRAUCH, C. Beiträge zur Kenntniss der ungeformten Fermente in den Pflanzen. 32 pp.
- KRAUSE, A. Zur Geschichte der Paraphenylendiamine. 20 pp.
- LIETZENMAYER, O. Ein Beitrag zur Kenntniss der Chelidonsäure und Aepfelsäure. 67 pp.
- LUTZ, R. Ueber Nitro- und Amido-Derivate des Chloreyms. 31 pp.
- MARTIN, P. Ueber Solanin und seine Zersetzungsproducte. 27 pp.
- PFAFF, S. Ueber die unlöslichen Bestandtheile der Kalke und Dolomite. 24 pp.
- PRELLE, A. Die Fettsäuren der Ziegenbutter. 26 pp.

#### ERRATA.

- P. 3, line 2 from bottom read "30 aq." for "0 aq."
- P. 34, line 10 from bottom, read "in" for "kein."
- P. 40, line 9 from bottom, insert "were performed" between "experiments" and "for."
- P. 53, line 23 from top, insert "of" between "formula" and "benzol."
- P. 54. The left-hand diagram at bottom should have only one short line projecting from each angle.

# AMERICAN CHEMICAL JOURNAL.

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## DETERMINATION OF NITROGEN IN THE ANALYSIS OF AGRICULTURAL PRODUCTS.\*

BY S. W. JOHNSON AND E. H. JENKINS.

In 1872, one of us found† that the mixture of caustic soda and caustic lime known as "soda-lime," and used in chemical analysis to determine nitrogen quantitatively, might be replaced by a much more easily prepared mixture of equal volumes of dry sodium carbonate and slaked lime. There is some difficulty in obtaining sodium carbonate suitable for this use. The super-carbonate, which can be readily dried, often contains nitrogen, and the crystals of sal-soda that, after washing, are free from nitrogen, cannot be quickly dried to a *fine* powder. After various trials, the following process of preparing an effective soda-lime was devised:

Equal weights of sal-soda, in clean (washed) large crystals, and of good white and promptly-slaking quick-lime, are separately so far pulverized as to pass holes of  $\frac{1}{16}$  inch, then well mixed together, placed in an iron pot, which should not be more than half filled, and gently heated, at first without

\* From the Report of the Connecticut Agricultural Experiment Station for 1878 Communicated by the Authors.

† Amer. Chemist, vol. iii, p. 161.

stirring. The lime soon begins to combine with the crystal water of the sodium carbonate, the whole mass heats strongly, swells up, and in a short time yields a fine powder, which may then be stirred to effect intimate mixture and to dry off the excess of water, so far that the mass is not perceptibly moist and yet short of the point at which it rises in dust on handling. When cold it is secured in well-closed bottles or fruit-jars, and is ready for use.

During the past year a large number of comparative analyses have been made on bone-dust, dried blood, fish-scrap, guano, maize-meal, zein or maize-fibrin, and egg-albumin, using soda-lime obtained as above described, and soda-lime either prepared by ourselves according to the directions of Varrentrap and Will, obtained by purchase (Merck's) or kindly supplied by W. M. Habirshaw, Esq., Chemist to the New York State Agricultural Society. These analyses have proved that the new soda-lime gives perfectly satisfactory results in all cases when soda-lime can be employed, or, at least, results perfectly agreeing with those obtained by the help of the soda-lime as usually prepared. It is not needful to adduce analyses here in support of this statement, since its truth will appear from the soda-lime combustions to be shortly given, all of which were made with this new mixture.

This soda-lime is to be recommended for the reasons that the materials for making it, sodium monocarbonate and quick-lime, are everywhere procurable in a state of purity, the preparation of many pounds of the mixture may be accomplished in an hour or two with little trouble, and the resulting soda-lime is extremely convenient to use, not absorbing moisture in the mixing, and never swelling in the tube to obstruct it on application of heat.

The controversy that has been so actively prosecuted of late years as to the applicability of the soda-lime method of determining nitrogen to the analysis of albuminoid matters, has led us to review the entire subject as far as possible. It is well known to chemists that a number of experimenters, viz. Nowack, Seegen, Neneke, Liebermann, Voelcker, and Musso, have failed to obtain with the soda-lime method as high results on flesh, milk, and similar substances, as by the use of the so-called absolute method, in which the organic body is

burned with copper oxide and its nitrogen directly measured in the state of gas. Even Ritthausen, who has stoutly maintained the correctness of the soda-lime method, having employed it in his elaborate researches on the vegetable albuminoids, has very recently admitted that it fails to give all the nitrogen of some of this class of bodies, and has fallen back on the absolute method as the only one to be depended upon.

Since it is a matter of high importance in agricultural and physiological work to use the most exact and especially the most trustworthy methods, we have endeavored to investigate the correctness of both modes of analysis, to study the sources of error to which they are severally subject, and to learn what is essential to bring out the greatest accuracy they are susceptible of.

We have been led to the conclusion that with the substances above named, both methods when properly worked give nearly accordant results. Dried blood, dried white of egg and maize-fibrin (crude, obtained by Ritthausen's methods) containing 12 or more per cent. of nitrogen, have yielded us from one to two-tenths of a per cent. less of nitrogen by the soda-lime combustion than by the absolute method. Our observations satisfy us, moreover, that this discrepancy is no more due to any fault of the soda-lime process than to the errors of the absolute method ; errors caused, probably, by the impossibility of removing the last traces of common air from the mixture, either by long-continued transmission of pure carbonic gas or by exhaustion with the Sprengel mercury pump, or by both conjointly.

The following results of analyses by both methods are offered to sustain our assertions. We have not selected these analyses to establish the point, but give all the results we have obtained since learning the best mode of conducting the analytical processes, and they fairly represent what the two methods can accomplish when applied with suitable precautions :

	By the Absolute Method.	By Soda lime.	Average difference.
Egg Albumin,	{ 12.54 per cent.	12.34 per cent.	.17 per cent.
	{ 12.51    "	12 36    "	
	{ 12.56    "	12 38    "	
	{ 12 44    "		
	{ 12.59    "		

	By the Absolute Method.		By Soda-lime.		Average difference.
Maize Fibrin (crude)	13.73 per cent.		13.60 per cent.		.13 per cent.
Dried Blood,	{ 11.90	"	11.78	"	.12 "
	{ 11.91	"	11.73	"	
" "	{ 7.54	"	7.58	"	.04 "
	{ 7.54	"	7.58	"	
Fish Scrap,	{ 9.21	"	9.12	"	.14 "
	{ 9.21	"	9.02	"	
" "	{ 8.79	"	8.64	"	.11 "
	{ 8.79	"	8.71	"	
Peruvian Guano,	{ 8.27	"	8.21	"	.06 "
	{ 8.63	"	8.49	"	
" "	{ 8.66	"	8.51	"	.15 "
	{ 8.21	"	8.13	"	
" "	{ 8.21	"	8.04	"	.12 "
	{ 9.68	"	9.63	"	
" "	{ 9.68	"	9.67	"	.03 "
	{ 7.56	"	7.56	"	
" "	{ 7.56	"	7.56	"	.00 "
	{ 7.56	"	7.56	"	

The above analyses illustrate a fact which is general in our experience, viz. that the agreement of several determinations made upon one substance is usually closer by the soda-lime than by the absolute method. This fact goes far to show that the soda-lime process is, to say the least, equal in accuracy with the absolute determination.

The full details of the mode we follow in making an analysis by the absolute method cannot be given here. An outline of the process is as follows :

The substance, mixed with *freshly ignited* copper oxide, is burned in a long glass tube which has been exhausted by means of a mercury pump ; the products of combustion after passing over ignited metallic copper, and *finally over ignited copper oxide*,\* are collected in a graduated receiver, containing fifty per cent. solution of caustic potash, and surrounded by a water-jacket. Complete combustion is ensured by heating, in due course, several grams of potassium chlorate at the rear of the tube, three inches of which is bent downward from the horizontal to retain the fused salt. The residual gas is trans-

\* The use of a short layer of oxide of copper at the anterior end of the tube was adopted by the writer in 1873, when making analyses of Connecticut tobacco, he having found it impossible to make a blank combustion when using carbonic acid to sweep the tubes, without obtaining unabsorbed gas in the receiver, which proved to be combustible. By burning this gas in the analysis, he was able to get results on uric acid and potassium ferrocyanide agreeing closely with theory and with those obtained by the soda-lime method. More recently, Frankland has adopted this use of copper oxide in nitrogen estimations for water analysis. S. W. J.

Since the above note was printed I have learned that Finkener, in his edition of Rose's Handbuch, anticipated me in this use of copper oxide. S. W. J.

ferred to the receiver by the pump, brought to a constant temperature by a stream of hydrant water and measured in the usual manner. The mercury pump employed is a very effective one, of simple and easy construction, devised for use in this kind of analysis.

With regard to the handling of the soda-lime method the following results have been arrived at:

1. Contrary to what is commonly stated, fine pulverization of the substance to be analyzed is not necessary. If the substance will pass holes of one millimeter in diameter it is fine enough.

A sample of dried blood which passed through a sieve with meshes one millimeter in diameter gave 7.58 per cent. of nitrogen. A portion of the same, ground extremely fine with sand, gave 7.64 per cent.

Fish-scrap passed through the same sieve gave 8.98 per cent. of nitrogen; when ground with sand, 8.95 per cent. A second sample of fish sifted as above gave 8.69 per cent. nitrogen. By the absolute method it yielded 8.79 per cent.

2. Neither the highest heat possible to obtain in an Erlenmeyer gas combustion furnace, nor a long layer of strongly heated soda-lime, nor these two conditions united, occasion any appreciable dissociation of the ammonia formed in combustion.

A sample of dried blood gave 11.42 per cent. of nitrogen when the combustion was made in a tube 14 inches long at a dull red heat.

The same sample yielded 11.56 per cent. when determined in a tube 30 inches long, the mixture occupying 12 inches, and the rinsings and clear soda-lime 16 inches, using as high a heat as possible.

The same experiment was tried with egg-albumin. In a tube 14 inches long it yielded 12.25 per cent.; in one 30 inches long, filled as above, 12.34 per cent.

A superphosphate containing animal matter yielded 3.02 per cent. of nitrogen when the heat was kept quite low, 3.04 per cent. when the heat during combustion was very bright red.

3. The use of pure sugar or of oxalic acid as a diluent does not in any way affect the result.

Dried Blood, 0.5 grams, gave.....	10.33	per cent. nitrogen.
“ “ with 0.5 grams sugar gave	10.29	“ “
“ “ “ 1.0 “ sugar “	10.08*	“ “
Dried Blood, “ gave .....	11.56	“ “
“ 0.37 grams with 1 gram sugar gave..	11.53	“ “
Egg Albumin, 0.5 “ gave.....	12.51	“ “
“ 0.4 “ with 0.5 grams sugar gave	12.41	“ “
“ 0.46 “ “ “ “	12.50	“ “
“ 0.3 “ “ “ “	12.54	“ “

Experiments with oxalic acid gave similar results.

4. Iron tubes *of proper length* may be substituted for glass. The results are as satisfactory, but more time is required to make the combustion.

The iron tubes used in the following trials were 22 inches long. They were closed at the rear, and at the end of the combustion were cleared of ammonia by heating a mixture of oxalic acid or sugar and soda-lime, which was kept cool in the rear of the tube till needed for this purpose.

	In glass.	In iron.
Egg Albumin.....	12.36	12.25 per cent nitrogen.
Dried Blood .....	11.42	11.56 “ “
Fish Scrap.....	9.01	8.99 “ “
“ .....	8.71	8.68 “ “
“ .....	8.66	8.72 “ “
Ammoniated Superphosphate ....	2.69	2.61 “ “
“ “ .....	2.71	2.68 “ “

In the Station Report for 1877 it was stated that combustions in iron tubes yielded 0.2 to 0.5 per cent. less than those in glass. This deficiency was occasioned simply by using too short an anterior layer of soda-lime, the tubes being but 14 inches long. Since iron is a good heat-conductor, these tubes had an effective length much less than glass tubes of the same dimensions would have.

5. A suitable length of the anterior layer of soda-lime must be secured in order to get a good result. With 0.5 gram of substances, such as are encountered in agricultural chemistry, containing less than 8 per cent. of nitrogen, a glass tube of 12 to 14 inches is long enough. As the content of nitrogen increases to 10 per cent. or over, we make the tubes several inches longer. In the combustion of dried blood or egg-albumin we *prefer* a tube 25 to 30 inches long, and the mixture of soda-lime and substance should occupy rather less than half

\* In this analysis the combustion was not complete, owing to the large amount of sugar being mixed with insufficient soda-lime.

the tube, a layer of pure soda-lime of 12 or more inches long being essential for perfectly destroying the volatile organic matters.

6. The long anterior layer of pure soda-lime must be brought to a *full red heat* before heating the mixture, and must be so kept throughout the combustion.

7. No fumes or tarry matters, indicative of incomplete combustion, should appear in bulb-tube or receiver.

8. When the combustion proper is begun under the conditions above described, it can be carried on quite rapidly until completed. The contents of the tubes then show no sign of unburned carbon.

9. We get equally good results whether the mixture is made intimately in a mortar, or more roughly by stirring with a spatula in a capsule or scoop, or by mixing in the tube with a wire.

10. We usually allow the glass tube to cool somewhat before aspirating with air to sweep out the ammonia, but have not as yet decided whether this precaution is essential.

11. We receive the ammonia of the combustion in a bulb-tube or flask containing standardized hydrochloric acid, and we measure the excess of acid by a standard ammonia solution, using tincture of cochineal as the indicator.

In conclusion, we recall the fact that some careful experimenters, Ritthausen, Märcker, Petersen, Kreusler, have repeatedly obtained results nearly as accordant as ours in the use of the two methods. Such results could scarcely be accidental, and we express our conviction that the discrepancies observed by others have been due to imperfect working of the processes. We have had great experience with both modes of determining nitrogen (one of us for twenty-five years), and not until recently have we learned how to be fairly certain of our results on *all* the classes of substances we have had occasion to analyze, either with the soda-lime process or by the absolute method. The purity and uniformly satisfactory qualities of the new soda-lime have greatly facilitated our work. The use of cochineal as an indicator we consider very favorable to exact titration.

ON A METHOD FOR THE DETERMINATION  
OF PHOSPHORIC ACID.\*

BY S. W. JOHNSON AND E. H. JENKINS.

Otto long ago proposed a method for the separation of phosphoric acid from iron and aluminum which was based on the fact that ammonium tartrate will prevent the precipitation of the hydrates and phosphates of these metals in alkaline solutions, but does not prevent the precipitation of ammonio-magnesium phosphate.

W. Mayer† has shown that unless a large amount of ammonium salts is present in solution, basic magnesium tartrate will also be precipitated with the phosphate. He prepared a solution for use in the determination of phosphoric acid in which the amounts of magnesium and ammonium salts were in such relation that a precipitation of basic magnesium tartrate was not to be feared. Such a solution cannot be used, however, for the direct gravimetric determination of phosphoric acid in the presence of much lime, because neutral calcium tartrate is apt to be precipitated with the ammonio-magnesium phosphate.

F. Stolba‡ has shown that pure ammonio-magnesium phosphate can be determined by titration as well as by weighing, one molecule of the pure salt requiring two molecules of hydrochloric acid to destroy its alkaline reaction. Advantage has been taken of these observations in devising a plan of operating which should meet the want felt for a rapid and accurate method of determining phosphoric acid in commercial fertilizers. The standard acid used in other volumetric work answers perfectly for this. A strong, nearly saturated, solution of ammonium tartrate, free from carbonic acid, and a solution of some magnesium salt, are also necessary. The latter is prepared by dissolving 70 grams of

\* From the Report of the Connecticut Agricultural Experiment Station for 1878. Communicated by the Authors.

† *Ann. Chem. Pharm.* 101, 164.

‡ *Zeitschr. Chemie*, xvi, 100.

magnesium sulphate and 195 grams ammonium chloride in 1 liter of water. 10 cubic centimeters of this solution contain twice the amount of magnesium necessary to precipitate 0.1 gram phosphoric acid ( $P_2O_5$ ). A suitable amount of the phosphate (in most cases 1 gram is a convenient quantity) is dissolved in hydrochloric acid, the solution nearly neutralized with ammonia, and ammonium tartrate solution is added, 10 cubic centimeters at a time, till the solution remains perfectly clear when slightly alkaline. Add a suitable quantity of the magnesium mixture, and either stir vigorously with a rod, or, if the precipitation is made in an assay-flask, as it can be very conveniently, shake occasionally. When the precipitation is nearly complete add enough ammonia to make it very strongly alkaline, and let it stand 6-12 hours. It can then be filtered, preferably on the pump, and washed with equal parts of strong alcohol, 85-90 per cent., and water. No pains are taken to detach the precipitate from the glass. When the dish and precipitate are washed until the washings no longer react alkaline, the filter and precipitate are brought back into the beaker or flask, a *little* water and a few drops of cochineal tincture are added, and it is titrated. This is best done by adding an excess of standard acid at once, stirring so that all the precipitate shall be wetted with it, and after it has stood a few minutes, measuring back with standard alkali.

The results given below (mostly duplicated) indicate the degree of accuracy to be expected.

			Determined by use of ammonium molybdate.	Determined by the method just described.
Superphosphates, soluble phosphoric acid,			8.92-8.96	8.83-8.91
"	"	"	8.31 . . . .	8.32
"	"	"	11.89-11.95	11.83-11.95
"	"	"	5.14-5.08	5.07-5.11
"	"	"	6.78 . . . .	6.68-6.84
"	"	"	5.63-5.65	5.61-5.63
"	total	"	9.21-9.28	9.22-9.32
"	"	"	10.70-10.72	10.76-10.87
*	"	"	16.66-16.66	16.55-16.65
*	"	"	13.94 . . . .	13.90-14.05
Hair Manure, . . .	"	"	2.23 . . . .	2.19 . . . .
Bone, . . . . .	"	"	21.90-21.90	21.87-21.75
" . . . . .	"	"	13.21-13.40	13.19-13.33
" . . . . .	"	"	22.57-22.62	22.57-22.76
" . . . . .	"	"	21.90-21.90	21.87-21.75
Fish Scrap, . . .	"	"	6.17-6.27	6.17-6.28

\* Navassa superphosphates containing soluble iron and aluminum phosphates.

	Calculated.	
Tricalcic phosphate with 6.44 per cent. water,	42.85	42.79
The above (0.5 gram) with 0.22 gram iron in form of ferric chloride . . . . .	42.85	42.79

In the case of a few phosphatic materials rich in phosphoric acid, larger discrepancies than any above given have been occasionally encountered, and it is proposed to give them further attention, although it is our impression that they were accidental and do not invalidate the accuracy of the method.

This process requires less than half the time and labor necessary for the molybdic method, is scarcely less accurate and appears to be generally applicable.

Some investigations, not completed as yet, lead us to hope that ammonium tartrate may be successfully substituted for ammonium citrate for bringing precipitated or reverted phosphates into solution. This step would still further simplify the analyses of superphosphates, since the entire phosphoric acid, soluble, reverted and insoluble, could be quickly estimated in a single portion.

Our investigations have also demonstrated that while ammonio-magnesium phosphate is totally insoluble in a large excess of ammonium tartrate, it is soluble in excess of ammonium citrate, and hence all methods based on the use of citric acid are faulty.

It is a fact also that ammonio-magnesium phosphate is largely soluble in ferric and aluminic solutions, containing *insufficient* ammonium tartrate.

It is therefore necessary in presence of iron to add ammonium tartrate more than enough to produce a reddish-yellow solution, enough in fact to make a greenish-yellow solution, as Otto has indicated. A similar excess of ammonium tartrate is also requisite in presence of aluminum, and while there is no color-indication of the suitable quantity, a large excess does not appear to retain ammonio-magnesium phosphate in solution, unless the liquids are too concentrated.



EXAMINATION OF THE NORTH CAROLINA  
URANIUM MINERALS.

BY F. A. GENTH.

Prof. W. C. Kerr describes the occurrence of uranium minerals in Mitchell County, North Carolina, as follows:\*

“A new locality, the Flat Rock mine, recently visited, has yielded the following in immediate association, viz. uraninite, gummite, uraconite, and, as incrustations on the outside of the latter, and of the fragments of rock adjacent, torbernite and autunite. These minerals occur only in one part of the mica-bearing portion of a very large granite vein, and are found in irregular nodules and rounded masses, some with a nucleus of uraninite of  $\frac{1}{2}$  to  $\frac{3}{4}$  inch, enveloped with a heavy layer of gummite, outside of which is a pale, yellow, earthy coating from  $\frac{1}{4}$  to  $\frac{1}{2}$  of an inch thick, which is uranochre or uraconite. One lump, the largest, weighs just a pound, and in all, I obtained between 3 and 4 pounds. The quantity of pitchblende, remaining unaltered is very small, and by far the greater part of the mass of the nodules, probably nine-tenths, is gummite; and the smaller ones are nearly or entirely changed to uraconite.”

Through the kindness of Prof. Kerr I have recently come into possession of specimens of this highly interesting occurrence, which fully agree with the description above quoted. As his mineralogical determinations, however, were not supported by chemical analysis, and, especially as the composition of gummite is very doubtful, I thought that an investigation of the uranium minerals from this locality would be desirable.

I regret that of the uraninite no material for analysis could be obtained. One of my specimens of gummite, however, still contains one or two small fragments of uraninite; the larger one has a brownish black color, on the margin changing into brownish and, by degrees, into the pure gummite. It is also penetrated by small veins, showing the gradual alteration of the uraninite.

\* Am. Journ. Sc. [3] xiv, 496.

*Uranotil*.—E. Boricky.

The analysis of the pale yellow coating surrounding the gummite shows that it is a variety of *uranotil*, and *not uranochre* or *uranoconite*. The original *uranotil* has been found in cavities of quartz, associated with fluorite at Wœlsendorf in Bavaria, in lemon-yellow, rhombic needles of a specific gravity of 3.95. For comparison I will give below Boricky's analysis of it.

The North Carolina variety is apparently amorphous; massive, compact.  $H = 2.5$ . Sp. gr. = 3.834. Lustre waxy to dull; color from pale straw-yellow to lemon-yellow; streak pale straw-yellow; opaque; fracture uneven.

B. B. in a tube yields water and becomes brownish yellow; with fluxes the uranium reactions. Easily soluble in chlorhydric acid; on evaporation yields a jelly of silicic acid.

The analyses gave, after deducting a small quantity of quartz, mica and feldspar:

				Mean.	Boricky.	Calculated.
SiO <sub>2</sub>	=	13.55 ... 13.88	...	13.72 ...	13.78 ...	13.95
Al <sub>2</sub> O <sub>3</sub> & Fe <sub>2</sub> O <sub>3</sub>	=	traces ... traces	...	traces ...	0.51 ...	.....
UO <sub>3</sub>	=	66.76 ... 66.59	...	66.67 ...	66.75 ...	66.98
PbO	=	0.74 ... 0.45	...	0.60 ...	...	...
BaO	=	0.28	} ... 0.48	0.28	...	...
SrO	=	0.13		0.13	...	...
CaO	=	6.23 .. 7.11	...	6.67 ...	5.27 ...	6.51
P <sub>2</sub> O <sub>5</sub>	=	not det'd	0.29 ...	0.29 ...	0.45 ...	...
H <sub>2</sub> O	=	not det'd	12.02 ...	12.02 ...	12.67 ...	12.56
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
			100.82	100.38	99.43	100.00

Rammelsberg\* gives for *uranotil* the formula  $\text{Ca}_2(\text{UO}_2)_6\text{Si}_5\text{O}_{18} + 15\text{H}_2\text{O}$ . My analyses agree far better with the following formula  $\text{Ca}_3(\text{UO}_2)_6\text{Si}_6\text{O}_{21} + 18\text{H}_2\text{O}$ , as will be seen from the above calculated analysis. It forms an incrustation upon gummite and results from its alteration, sometimes (as has been observed by Prof. Kerr) changing the entire mass of the latter and yielding nodules of pure *uranotil*; mostly, however, converting not only the outside of the gummite into *uranotil*, but penetrating its whole mass, so that even the purest particles contain already a large percentage of it, as will be seen from the analyses of the gummite.

\* Mineralchemie, 692.

*Gummite.*

The orange-colored mineral from the Flat Rock mine has been called gummite, from its resemblance to that from European localities. It occurs in amorphous, compact, nodular masses.  $H = 3$ . Sp. gr. = 4.840. Lustre faintly resinous to dull; color reddish yellow to deep orange red; streak orange yellow; opaque; fracture subconchoidal to uneven.

B. B. yields water and turns reddish brown; upon charcoal with sodium carbonate yields metallic lead, with fluxes gives the reactions of uranium. Easily soluble in acetic acid.

Below I give the analyses of the purest, deep orange red material, after deducting a minute quantity of quartz, feldspar and mica. For comparison I add the only analysis which is known of gummite, that from Johann-Georgenstadt in Saxony, by Kersten:

					Mean.	Johann-Georgen- stadt, Kersten.	
SiO <sub>2</sub>	=	4.49 ...	4.83 ...	4.58 ...	4.63	...	4.26
Al <sub>2</sub> O <sub>3</sub>	=	0.67 ...	0.40	} [4.59] }	0.53	Mn <sub>2</sub> O <sub>3</sub>	0.05
BaO	=	0.98	} 1.12		1.08	As, Fl traces.	
SrO	=	0.05				...	...
CaO	=	1.96 ...	2.14	...	2.05	...	6.00
PbO	=	5.48 ...	5.58 ...	5.64 ...	5.57	...	...
UO <sub>3</sub>	=	[75.71]...	75.50 ...	74.39 ...	75.20	...	72.00
P <sub>2</sub> O <sub>5</sub>	=	0.12 ...	0.07 ...	0.16 ...	0.12	...	2.30
H <sub>2</sub> O	=	not det'd	10.43 ...	10.64 ...	10.54	...	14.75
		<hr/>		<hr/>		<hr/>	
		100.07		99.72		99.36	

The opinion of chemists as to the composition of gummite is very much divided. Kersten thought it to be a combination of phosphate of lime with uranic hydrate, the composition of which he expressed by the formula  $3\text{CaO}, \text{P}_2\text{O}_5 + 4\text{U}_2\text{O}_3, 9\text{H}_2\text{O}$ . Berzelius considered it as a mixture of basic phosphate and basic silicate of uranic oxide and lime. Hausmann takes it to be principally the hydrate of uranic oxide. Rammelsberg expresses the same opinion, but believes that the analyses of gummite, together with those of eliasite and pittinite, represent mixtures, and that from their analyses no rational composition can be derived. Hermann, on the other hand, considers these and other uranium minerals, in which silicic acid has been

found, even uraninite, as definite compounds of the formula:  $4\text{RO}, \text{SiO}_2 + 4(4\text{R}_2\text{O}_3, \text{SiO}_2) + m\text{H}_2\text{O} + n\text{X}$ . The accessory molecule X being wanting in pittinite, and in the other species represented by  $\text{R}(\text{AsS})$  in uranochalcite, by  $4\text{RO}, \text{U}_2\text{O}_3$  in uraninite, by  $\text{CaO}, \text{CO}_2$  in eliasite, by  $3\text{CaO}, \text{P}_2\text{O}_5$  in phosphor-gummite, and by  $3\text{CaO}, (\text{PV})_2\text{O}_5$  in vanadin-gummite. Hermann's views are as untenable as those of the others. Nearest to the truth, in my opinion, comes Patera, who holds that silicic acid and phosphoric acid are not essential, and that gummite is principally a lime-uranate,  $\text{CaO}, 2\text{U}_2\text{O}_3 + 6\text{H}_2\text{O}$ , analogous in composition to the artificial uran-yellow.

Gummite is the result of an alteration of uraninite, and it seems to me that both pittinite and eliasite are intermediate between the two, containing more or less of either. But I have already pointed out the fact that the gummite from North Carolina is a mechanical mixture, and that uranotil penetrates the whole mass. The gradual change from gummite into uranotil can be observed on every specimen from this locality.

If we calculate from the  $\text{SiO}_2$  in the gummite the requisite constituents of uranotil, making up the minute deficiency of  $\text{CaO}$  by its equivalent of  $\text{BaO}$ , we get:

$\text{SiO}_2$	=	4.63
$\text{CaO}$	=	2.05
$\text{BaO}$	=	0.30
$\text{H}_2\text{O}$	=	4.17
		<hr/>
		33.38 per cent. of uranotil.

The  $\text{PbO}$  and  $\text{BaO}$  may be most rationally considered as being present in the form of  $\text{M}(\text{UO}_2)_2\text{O}_3 + 6\text{H}_2\text{O}$ ; we get therefore

$\text{PbO}$	=	5.57
$\text{UO}_3$	=	14.39
$\text{H}_2\text{O}$	=	2.70
		<hr/>
		22.66 per cent. of lead-uranate; and
$\text{BaO}$	=	0.78
$\text{UO}_3$	=	2.93
$\text{H}_2\text{O}$	=	0.55
		<hr/>
		4.26 per cent. of barium-uranate.

There remain 35.65 per cent. of  $\text{UO}_3$ , which is evidently present as uranic hydrate, requiring 4.45 per cent. of water.

The gummite from the Flat Rock mine is therefore a mechanical mixture of:

Uranic hydrate	=	$\text{H}_2(\text{UO}_2)\text{O}_2 + \text{H}_2\text{O}$	=	40.10 %
Uranotil	=	$\text{Ca}_3(\text{UO}_2)_6\text{Si}_6\text{O}_{21} + 18\text{H}_2\text{O}$	=	33.38
Lead-uranate	=	$\text{Pb}(\text{UO}_2)_2\text{O}_3 + 6\text{H}_2\text{O}$	=	22.66
Barium-uranate	=	$\text{Ba}(\text{UO}_2)_2\text{O}_3 + 6\text{H}_2\text{O}$	=	4.26
				<hr/>
				100.40

The analyses of pittinites and eliasites admit of no calculation as they appear to have too many foreign substances present, and as the amount of uranous oxide which they evidently contain has not been determined; if we take the analysis of gummite from Johann-Georgenstadt, we find it probably to be a mixture of calcium-uranate, with uranotil, a uranium-phosphate (phosphuranylite) and uranic hydrate. These calculations give the following amounts:

$\text{SiO}_2$	=	4.26
$\text{UO}_3$	=	20.45
$\text{CaO}$	=	1.99
$\text{H}_2\text{O}$	=	3.84
		<hr/>
		30.54 per cent. of uranotil.

$\text{CaO}$	=	4.01
$\text{UO}_3$	=	41.25
$\text{H}_2\text{O}$	=	7.73
		<hr/>
		52.99 per cent. of calcium-uranate.

$\text{P}_2\text{O}_5$	=	2.30
$\text{UO}_3$	=	4.68
$\text{H}_2\text{O}$	=	1.75
		<hr/>
		8.73 per cent. of phosphuranylite.

$\text{UO}_3$	=	5.62
$\text{H}_2\text{O}$	=	0.70
		<hr/>
		6.32 per cent. of uranic hydrate.

The gummite from Johann-Georgenstadt has therefore probably the following composition, corresponding with Kersten's analysis :

Uranic hydrate	=	$H_2(UO_2)O_2 + H_2O$	=	6.32 %
Uranotil	=	$Ca_3(UO_2)_6Si_6O_{21} + 18H_2O$	=	30.54
Phosphuranylite	=	$(UO_2)_3P_2O_8 + 6H_2O$	=	8.73
Calcium-uranate	=	$Ca(UO_2)_2O_3 + 6H_2O$	=	52.99
				<hr/>
				98.58

*Phosphuranylite*.—A new species.

Rhombic (?). Under the microscope very minute rectangular scales with pearly lustre can be distinguished. In pulverulent incrustations upon quartz, feldspar and mica. Color deep lemon-yellow.

B. B. in the tube yields water and becomes reddish brown while hot, brownish yellow after cooling; readily soluble in nitric acid, yielding with ammonium molybdate a yellow precipitate; contains *no* arsenic acid.

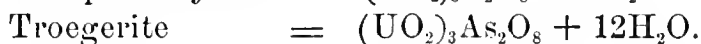
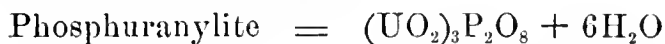
As this mineral is very rare, only a very minute quantity could be obtained which was free from autunite; this being in the form of a thin coating upon quartz, both together had to be taken as material for analysis.

0.6705 grams contained 0.5617 grams quartz—the analysis was therefore made with 0.1088 grams of material. This was slightly mixed probably with cerussite, which was visible under the microscope in the form of very small colorless particles. In the first column I give the results of the analysis, in the second the percentage of the phosphate, excluding the lead oxide, and in the third the calculated percentage, corresponding to the formula given below.

					Calculated.	
UO <sub>3</sub>	=	71.73	...	76.71	...	77.56
PbO	=	4.40	...	...	...	...
P <sub>2</sub> O <sub>5</sub>	=	11.30	...	12.08	...	12.75
H <sub>2</sub> O	=	10.48	...	11.21	...	9.69
		<hr/>		<hr/>		<hr/>
		97.91				

It will be seen from this analysis that the uranium and phosphorus are present exactly in the ratio of 3 : 2, and that

the composition of phosphuranylite may be expressed by a formula analogous to that of troegerite, but containing only half the amount of water :



Prof. Kerr mentions torbernite as one of the uranium minerals from the Flat Rock mine, and he sent me some uranite, which had a deep green color and resembled it very closely; but the chemical examination of one of the darkest green crystals showed that it contained only lime, and not a trace of copper oxide, and that the uranite from this locality is therefore only autunite.

UNIVERSITY OF PENNSYLVANIA, W. Philadelphia, April 12, 1879.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

No. I.

### RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.\*

BY C. LORING JACKSON.

#### INTRODUCTION.

The existence of the benzyl compounds was first established by Cannizaro,† in 1853; for, although Liebig and Wöhler,‡ in their classical research on the benzoyl compounds, obtained benzylalcohol as a secondary product from the action of potassic hydrate on benzaldehyde, they merely spoke of it as an oily liquid, and did not determine its composition or properties. It was also Cannizaro who, in 1855,§ showed that

\* Presented to the American Academy of Arts and Sciences. Communicated by the author.

† Ann. der Chemie, 88, p. 129.    ‡ Ib., 3, p. 249.    § Ib., 96, p. 246.

toluole, when treated with chlorine, yielded a substance identical with the benzylchloride prepared from benzylalcohol by means of hydrochloric acid. The nature of the action of chlorine on toluole was not, however, thoroughly understood until Beilstein and Geitner,\* in 1866, found that chlorine converted cold toluole into chlortoluole, but yielded benzylchloride with boiling toluole. In the same paper they predicted that pure chlorbzylchloride could be prepared by the action of chlorine either on hot chlortoluole or on cold benzylchloride. Both these methods were tried successfully by Neuhof† in the same year, but the chlorbzylchloride thus obtained was not the first substituted benzyl compound known, as Beilstein‡ had already obtained the chlorbzylmercaptan, and Naquet§ the chlorbzylethylether, from the mixture of dichlortoluoles made by acting upon toluole with chlorine. Immediately after the preparation of chlorbzylchloride by Neuhof, many of its derivatives were studied by Beilstein and Kuhlberg and Neuhof;|| and the two former extended their investigations to the chlorbzyl compounds containing more than one atom of chlorine attached to the benzole ring. Since that time, but little attention has been given to this class of compounds; the only researches being those of Böhler,¶ and later, Vogt and Henninger,\*\* on the sulphoacids, of Berlin,†† who obtained some curious results from the animes, of Sintenis,‡‡ who investigated the ethers, and of Pauly on the sulphide.§§

Besides these chlorbzyl compounds, only two other classes of substances lying within the range of this paper have been studied, the nitrobenzyl compounds—the first of which, nitrobenzylchloride, was described by Beilstein and Geitner in 1866, in the papers already referred to;||| its derivatives were further studied by Grimaux,¶¶ Beilstein, and Kuhl-

\* Beilstein and Geitner, *Ann. der Chemie*, 139, p. 331.

† Neuhof, *Zeitschr. der Chem.*, 1866, p. 653.

‡ Beilstein, *Ann. der Chemie*, 116, p. 346.

§ Naquet, *ib.*, Sup. 2, p. 250. *Compt. rend.*, 56, p. 129.

|| Beilstein, Kuhlberg, Neuhof, *Ann. der Chemie*, 147, p. 339; *ib.*, 150, p. 286; *ib.*, 146, p. 319.

¶ Böhler, *Ann. der Chemie*, 154, p. 56.

\*\* Vogt, Henninger, *Ann. Chim. Phys.* [4], 27, p. 130; *Ann. der Chemie*, 165, p. 362.

†† Berlin, *Ann. der Chemie*, 151, p. 137.

‡‡ Sintenis, *ib.*, 161, p. 329.

§§ Pauly, *ib.*, 167, p. 187.

||| Beilstein and Geitner, *Ann. der Chemie*, 139, p. 331.

¶¶ Grimaux, *Compt. rend.*, lxx., p. 211; *Ann. der Chemie*, 115, p. 46.

berg,\* Böhler,† Strakosch,‡ Czumpelik,§ Radziszewski,|| Henry,¶ and Jackson,\*\* and a few amidobenzyl compounds, the cyanide prepared by Czumpelik,†† and the animes by Strakosch.‡‡

All these substances belonged to the para series, and no isomeric chlor- or nitrobenzyl compounds were known with the exception, perhaps, of the monochlorbenzylsulphosalts described by Vogt and Henninger,§§ and the isomeric nitrobenzylalcohol obtained by Grimaux|||| from nitrobenzaldehyde, until 1876, when the meta- and orthobrombenzylbromides were described in a preliminary notice ¶¶ of a portion of the work contained in these papers. In 1877 Wachendorff published a very interesting paper\*\*\* upon the nitrobenzylchlorides and bromides, in which he described the metanitrobenzylbromide, and called attention to the striking facts that metanitrobenzylchloride could not be obtained under conditions which gave without difficulty the paranitrobenzylchloride, and he had not as yet succeeded in obtaining the ortho compounds under any of the conditions which furnished their isomeres.

#### ON CERTAIN SUBSTITUTED BENZYL BROMIDES.

*Parabrombenzylbromide* ( $C_6H_4Br.CH_2Br$ ). — Preparation. First Method. Ten grams of pure parabromtoluole, melting point  $28.5^\circ$ , (either from the factory of Kahlbaum in Berlin, or of Schuchardt in Gœrlitz) were heated in a paraffine-bath to the boiling-point of parabromtoluole in a small flask, through whose cork passed a return-cooler and the stem of a drop-funnel containing 10 grams of bromine, the end of which within the flask was less than a centimeter above the surface of the bromtoluole; the bromine was allowed to flow in at such

\* Beilstein, Kuhlberg, Neuhof, Ann. der Chemie, 147, p. 329; ib., 150, p. 286; ib., 146, p. 319.

† Böhler, Ann. der Chemie, 154, p. 55.

‡ Strakosch, Ber. d. chem. Gesell., 1872, p. 692.

§ Czumpelik, ib., 1870, p. 473.

|| Radziszewski, ib., 1870, p. 198.

¶ Henry, ib., 1869, p. 637.

\*\* Jackson, ib., 1875, p. 321.

†† Czumpelik, ib., 1870, p. 473.

‡‡ Strakosch, ib., 1872, p. 692.

§§ Vogt, Henninger, Ann. Chim. Phys. [4], 27, p. 139; Ann. der Chemie, 165, p. 362.

|||| Grimaux, Compt. rendus, lxx., p. 211; Ann. der Chemie, 145, p. 46.

¶¶ Jackson, Ber. d. chem. Gesell., 1876, p. 931.

\*\*\* Wachendorff, Ann. der Chemie, 185, p. 259.

a rate that it was completely decolorized at a short distance from the end of the tube. If these precautions were observed, the liquid solidified almost completely on cooling, and the substance was easily purified by pressing the crystals thus obtained between filter-paper and recrystallizing once or twice from hot alcohol. The average yield from ten grams of parabromtoluole was ten grams of parabrombenzylbromide, that is about sixty-eight per cent. of the theoretical amount; as the method of purification given above is attended with some loss from the formation of an ethylether it is better, if large quantities of the substance are needed, to distil the product of the reaction with the vapor from an aqueous solution of hydrobromic acid, which gives, after pressing on filter-paper, a product pure enough for ordinary preparation work.

The substance was also obtained from the mixture of para- and orthobromtoluole,\* prepared by treating cold toluole with bromine. On cooling the product of the action of bromine on the hot mixture with ice and salt, some parabrombenzylbromide separated out, and more was obtained by distilling off a part of the oil with hydrobromic acid and steam, as the orthobrombenzylbromide distils over more easily than the para compound. This method is not to be recommended, however.

Second Method. Benzylbromide was treated in the cold with an equal weight of bromine, to which a little iodine had been added; on freezing the product of the reaction, a quantity of parabrombenzylbromide separated out. This method is decidedly inferior to that with pure parabromtoluole, as it not only gives a smaller yield, but also there is a possibility that orthobrombenzylbromide may be formed.

The composition of the parabrombenzylbromide was established by the following analyses:

0.5934 gr. of substance gave 0.7377 gr.  $\text{CO}_2$  and 0.1378 gr.  $\text{H}_2\text{O}$ .

0.5679 gr. of substance gave, after ignition with  $\text{CaO}$ , 0.8579 gr.  $\text{AgBr}$ .

	Required for $\text{C}_7\text{H}_6\text{Br}_2$ .	Found.
Carbon	33.6	33.90
Hydrogen	2.4	2.57
Bromine	64.0	64.28
	<hr/> 100.0	<hr/> 100.75

\*Ann. der Chemie, 147, p. 39.

*Properties.*—Crystallized from alcohol, it forms thick colorless needles, with a brilliant lustre; from the oily mother-liquor formed in its preparation or from benzole, it separates on slow evaporation in well-formed prisms, apparently of the orthorhombic system, often a centimeter or more long and two to four millimeters thick, which have the consistency of sublimed sal-ammoniac. Its odor is agreeable and aromatic, but its vapor attacks the mucous membrane with very great violence, causing tears, and running at the nose; it was observed, however, by all who were exposed continually to its action that they became much less sensitive to it after a few days. When brought upon the more delicate parts of the skin it causes a sharp, stinging pain, but produces no such effect on the hands; the taste is extremely biting, causing great pain to the tongue for several minutes; it melts at  $61\frac{1}{4}^{\circ}$ , can be distilled with steam, sublimes in needles, and burns with a luminous green-bordered flame. It is almost insoluble in water, although it imparts its odor to it; (the flat needles, mentioned in a preliminary paper\* as separating from water by spontaneous evaporation, were undoubtedly the more soluble parabrombenzylalcohol); it is but slightly soluble in cold, freely in hot alcohol, very readily in ether, benzole, carbonic disulphide, and glacial acetic acid. On one occasion it was oxidized very rapidly by a mixture of potassic dichromate and dilute sulphuric acid, the action being attended by flashes of light visible even in diffused daylight, the product was an acid melting in the crude state at  $239^{\circ}$  to  $240^{\circ}$ , which must therefore be parabrombenzoic acid.

It seems highly probable that this parabrombenzylbromide is the substance obtained, but not purified or studied by Lauth and Grimaux,† in 1866, in the residue from the distillation of bromtoluole; since they described it as crystallizing in needles, and in the highest degree irritating to the eyes.

*Metabrombenzylbromide* ( $C_6H_4^mBr.CH_2Br$ ) was made from metabromtoluole, prepared by Wroblevsky's‡ method (compare also Grete§), as follows: 30 gr. of the mixture of para- and orthoacettoluid, obtained as a secondary product in Wroblev-

\* Ber. d. chem. Gesell., 1876, p. 931.

† Lauth and Grimaux, Bull. Soc. chim. [2], v. p. 347.

‡ Wroblevsky, Ann. der Chemie, 168, p. 153.

§ Grete, ib., 177, p. 231.

sky's process for purifying orthotoluidine, previously reduced to a granular condition by crystallization from boiling water, were suspended in cold water, and 45 gr. of bromine dissolved in water added in small portions at a time, shaking until the yellow color disappeared after each addition; the acetyl group was removed from the metabromacetoluid thus obtained by boiling with fuming hydrochloric acid in a flask with a return cooler; the base, set free by an alkali, was dissolved in portions of 10 gr. at a time in absolute alcohol, and the amido group replaced by hydrogen by Griess's reaction; the alcohol was then partly distilled off on the water-bath; the residue distilled with steam, dried, and rectified, the portion passing over from  $179^{\circ}$  to  $185^{\circ}$  being collected. To convert this into metabrombenzylbromide, 10 gr. of it were heated to boiling, and treated with 10 gr. of bromine in the way described under parabrombenzylbromide (see page 95); the metabromtoluole took up the bromine somewhat more slowly than the parabromtoluole. The liquid left after the bromining was finished was distilled in a current of the vapor from hydrobromic acid (boiling point  $125^{\circ}$ ), prepared according to Naumann,\* until a considerable portion had passed over: the flask containing the substance was not heated for fear of decomposition. The hydrobromic acid vapor cannot be replaced by steam; as under these conditions some of the brombenzylalcohol might be formed, although I am inclined to think that this reaction would take place much less readily here than it does in the case of the parabrombenzylbromide. The residue left in the flask was transferred to a funnel-tube, closed with a rubber stopper on a glass rod and surrounded with ice. If the distillation had been carried on long enough, nearly the whole of the oil solidified to a dark, pasty mass. The stopper was then removed, and the brown oil sucked out as completely as possible by means of the Bunsen pump. The white scales left on the funnel were boiled with a small quantity of alcohol; the clear solution poured off from the undissolved oil and cooled in a corked flask. As soon as no more oil was deposited the clear liquid was decanted into another flask and cooled with ice, when crystals were formed. The same process was repeated with the mother-liquor and the residue until the whole

\* Naumann, Ber. d. chem. Gesell., 1876, p. 1574.

was converted into crystals; another crop of less pure metabrombenzylbromide was obtained by adding snow to the mother-liquor from the final operation. The crystals were purified by similar crystallization from hot alcohol. It was necessary that all these operations should be carried on in corked flasks, as the metabrombenzylbromide, when moistened with alcohol, evaporated when exposed to the air so rapidly that there was a very considerable loss from working with open vessels.

The composition of the metabrombenzylbromide was established by analysis:

0.4333 gr. substance gave, after ignition with CaO, 0.6609 gr. AgBr.

	Required for $C_7H_6Br_2$ .	Found.
Carbon	33.6	34.63
Hydrogen	2.4	2.66
Bromine	64.0	63.96
	<hr/> 100.0	<hr/> 101.25

*Properties.*—Crystallized from alcohol by cooling, it forms white bladed needles or plates arranged in radiated groups; by slow evaporation of its alcoholic solution, it can be obtained in flat prisms with square ends sometimes reaching a length of 3 cm. and a breadth of 2 mm. It has an agreeable odor, aromatic, but different from that of parabrombenzylbromide, while its action on the mucous membrane is even more violent, perhaps because it is more volatile; its taste and action on the more delicate parts of the skin is similar to that of the para compound; it melts at  $41^\circ$ , can be distilled with steam only very slowly, sublimes in oily drops, and burns with a luminous flame having a green border. One of its most striking properties is that when moistened with alcohol or ether it evaporates very rapidly, whereas when dry it is comparatively fixed. It is almost insoluble in water, but imparts its odor to it, is freely soluble in cold, still more so in hot alcohol, and very readily soluble in ether, benzole, carbonic disulphide, and glacial acetic acid. An oxidizing mixture of potassic dichromate and dilute sulphuric acid seems to be without action on it; but the same mixture converts the alcohol derived from it into an acid, which, in a not perfectly pure state, melted at  $151^\circ$ , and must therefore be metabrombenzoic acid.

*Orthobrombenzylbromide* ( $C_6H_4Br.CH_2Br$ ).—After several unsuccessful attempts to obtain an orthobromtoluole free from the para compound from the mixture prepared by adding bromine to cooled toluole, I decided to insure a perfectly pure substance as my starting-point by making the orthobromtoluole from orthotoluidine. The first method employed for purifying the orthotoluidine was that of Wroblevsky,\* by boiling crude toluidine sixteen hours with glacial acetic acid; but all the samples obtained by this process contained traces of paratoluidine. After I had convinced myself by experiment that the methods of Rosenstiehl,† by treating the oxalates with ether; and of Beilstein and Kuhlberg,‡ by precipitating an acetic acid solution of acettoluid with water,—were almost impracticable for large quantities, I tried the method of Schad,§ recommended by Kekulé,|| which depends on the crystallization of the nitrates and chlorides, and in this way succeeded in obtaining a liquid toluidine which with acetylchloride gave an acettoluid melting after one recrystallization from boiling water at  $107^\circ$ . As some previous attempts to convert orthotoluidine into orthobromtoluole by the usual method through the diazoperbromide had given me as unsatisfactory a yield as that obtained by Wroblevsky,¶ I treated this according to a new modification of the process of Huebner and Majert\* for preparing parachlortoluole, which I had found to work admirably in making that substance. This modification was suggested by Victor Meyer's†† method of applying Griess's reaction, and consisted in dissolving 20 gr. of the orthotoluidine in an excess of hydrobromic acid (boiling point  $125^\circ$ , prepared according to Naumann‡‡); the pasty mass was then treated with somewhat more than the calculated amount of solid potassic nitrite, which was added in small portions at a time, the flask being corked after each addition, and shaken until all the red fumes were absorbed; after the last portion of nitrite had been added, the greater

\* Wroblevsky, *Ann. der Chemie*, 168, p. 162.

† Rosenstiehl, *Zeitschr. Chem.*, 1868, p. 557, 666.

‡ Beilstein, *Ann. der Chemie*, 156, p. 75.

§ Schad, *Ber. d. chem. Gesell.*, 1873, p. 1361.

|| Kekulé, *Ber. d. chem. Gesell.*, 1874, p. 1006.

¶ Wroblevsky, *Ann. der Chemie*, 168, p. 171.

\* Huebner and Majert, *Ber. d. chem. Gesell.*, 1873, p. 794.

†† V. Meyer, *Ber. d. chem. Gesell.*, 1875, p. 1074, note.

‡‡ Naumann, *Ber. d. chem. Gesell.*, 1876, p. 1574.

part of the liquid was distilled off, and the residue then treated again in the same way. The distillate consisted of dilute hydrobromic acid and a heavy oily liquid which was separated with a drop-funnel, washed with potassic hydrate solution until the odor of cresole was removed, then with water, and finally dried and rectified; in this way 40 grams of orthotoluidine gave 29 grams of crude orthobromtoluole, and 24 grams of this gave on the first fractioning 19 grams of a colorless liquid boiling between  $179^{\circ}$  and  $182^{\circ}$ ; that is, about thirty-six per cent. of the theoretical yield, whereas the diazoperbromide furnishes under the best conditions only ten per cent. The new method has the further advantages of taking much less than half the time occupied by either of the old ones, and the product is not contaminated with the nitro compounds which compelled Huebner and Majert to reduce before rectifying. Von Richter\* has also obtained tetrabrombenzole by the action of nitrous anhydride on a mixture of tribromaniline with hydrobromic and glacial acetic acids; he ascribes the reaction to the presence of the negative atoms, and announces his intention of trying similar experiments with compounds containing fewer bromine atoms or nitro groups; that the reaction is not due to the presence of such negative radicals is proved by the previous researches of Huebner and Majert, which he seems to have overlooked, and the results given above. I should not have intruded on von Richter's field of work had it not been necessary for me to obtain the orthobromtoluol, but I felt the less hesitation in doing so, as I am unable to see that his method differs in any essential particular from that of Huebner and Majert, published nearly two years before the appearance of his article.

The orthobromtoluole was converted into orthobrombenzylbromide by treatment with bromine in the way described under the para compound. The purification of the substance was a matter of some difficulty, as it seemed to be completely decomposed by rectification, and converted into the alcohol by distillation with steam; the method finally adopted was distillation in a stream of the vapor from aqueous hydrobromic acid, as described under the metabrombenzylbromide; the first fifth of the distillate was rejected to make sure of the

\* Von Richter, Ber. d. chem. Gesell., 1875, p. 1428.

absence of orthobromtoluole; that which came over later was washed till it ceased to give an acid reaction, and then dried *in vacuo*. In this way 17 grams of pure orthobrombenzylbromide were obtained from 18 grams of orthobromtoluole.

Its purity was established by the following bromine determination:

0.5035 gr. of substance gave, after ignition with CaO, 0.7608 gr. of AgBr.

	Required for $C_7H_6Br_2$ .	Found.
Bromine	64.0	64.30

A number of bromine determinations made in products from distillation with steam gave invariably results which were below the theory.

*Properties.*—It forms a pale yellow oil (the color is undoubtedly due to a trace of some impurity), with an agreeable odor, somewhat resembling that of parabrombenzylbromide, and an action on the mucous membrane even more violent than that of the preceding compounds; its boiling point seems to lie between  $250^\circ$  and  $260^\circ$ , but could not be determined with accuracy because it is decomposed with evolution of hydrobromic acid by boiling. A careful study of the action of heat on this and the allied substances is reserved for a future paper. It does not solidify even at  $-15^\circ$ , can be distilled with steam, burns with the usual luminous green-bordered flame, and does not mix with water, although it imparts its odor to it, but mixes readily with absolute alcohol, ether, benzole, glacial acetic acid, and carbonic disulphide. It does not seem to be attacked by a mixture of potassic dichromate and dilute sulphuric acid, but the alcohol derived from it is completely destroyed by this oxidizing mixture.

*Parachlorbenzylbromide*,  $C_6H_4ClCH_2Br$ , was prepared from parachlortoluole; melting-point,  $6.5^\circ$ ; boiling point,  $158^\circ$ – $161^\circ$ ; made by the modification of the method of Hnebner and Majert, already described in connection with orthobromtoluole (see page 100); crude fuming hydrochloric acid took the place of the hydrobromic acid, and 40 gr. of paratoluidine were used for each operation; the oil, after washing with potassic hydrate, proved on rectification to be almost absolutely pure parachlortoluole, the yield being about 13 gr. It was converted into parachlorbenzylbromide in the way already described;

the product of the reaction deposited crystals on cooling, which were drained, and a fresh crop obtained from the mother-liquor by heating it gently for a few minutes in a watch-glass placed on a sand-bath, and then allowing it to stand for some time. The crystals after pressing between filter paper were purified by crystallization from hot alcohol in corked flasks, as the substance is so volatile that work in open vessels would have been attended with great loss; upon cooling the solution with ice, a little oil separated; and if the liquid was then stirred it immediately became filled with beautiful white needles.

The composition of the parachlorbenzylbromide was established by the following analyses:

0.3399 gr. of the substance gave, after ignition with CaO, 0.5580 gr. AgBr + AgCl.

0.4224 gr. of substance gave 0.6779 gr. AgBr + AgCl.

	Required for $C_7H_6Cl$ Br.	Found.	
Chlorine and Bromine	56.20	57.20	55.94

*Properties.*—By slow evaporation of its alcoholic solution it can be obtained in well-formed colorless prisms, by cooling in radiated bunches of needles often three centimeters long; it has an agreeable aromatic odor, and acts on the mucous membrane more violently than any of the other substances described in this paper; it melts at  $48\frac{1}{2}^\circ$ , sublimes in oily drops, can be distilled with steam, is very volatile at ordinary temperatures, so that a crystal will evaporate completely if exposed to the air for a few days, and burns with a flame similar to that of the bromine compounds. It is slightly soluble in water, easily soluble in cold, still more so in hot alcohol, and very readily in ether, benzole, carbonic disulphide, and glacial acetic acid. It is attacked with difficulty, if at all, by potassic dichromate and dilute sulphuric acid. This substance was made but not described by Pauly.\* It is highly probable, however, that he did not get it free from the ortho compound.

*Paraiodbenzylbromide*,  $C_6H_4ICH_2Br$ , was made from para-iodtoluole; melting point,  $35^\circ$ ; prepared according to Kœrner†

\* Pauly, Ann. der Chemie, 167, 187.

† Kœrner, Bull. Acad. Roy. Belg. [2]. 24. p. 157.

by the action of hydriodic acid on the nitrate of diazotoluole, this last being obtained by Victor Meyer's\* excellent modification of Griess's reaction. The introduction of the bromine into the side-chain by treating the boiling substance with bromine vapor was much more difficult than in the preceding cases; the precautions to be observed were in general the same as those given under parabrombenzylbromide; but occasionally, in spite of all possible care, a black tarry liquid was the only result of the process. The conditions under which the paraiodbenzylbromide is formed have been carefully studied by Mr. C. F. Mabery, and the results will be published in his paper upon the paraiodbenzyl compounds. It is a very remarkable fact that in several cases, when the paraiodtoluole was not perfectly pure, the liberation of iodine in considerable quantity was observed during the bromining; but in spite of this, the product contained paraiodbenzylbromide, thus apparently furnishing an exception to the general rule of Beilstein that, in presence of iodine, bromine goes into the benzole ring even at high temperatures. The product of the reaction, if properly managed, solidified on cooling, and was best purified by standing on paper, which sucked out a quantity of black oil, and afterward by repeated crystallizations from boiling alcohol with the assistance of bone-black.

The composition of the paraiodbenzylbromide was determined by the following analyses:

0.3721 gr. of substance yielded 0.3773 gr.  $\text{CO}_2$  and 0.0773 gr. of  $\text{H}_2\text{O}$ .

0.1774 gr. of substance gave, according to Carius, 0.1285 gr. of Ag.

0.1971 gr. of substance gave 0.2755 gr. of  $\text{AgBr} + \text{AgI}$ . There were indications in this analysis that the oxidation had not been complete.

	Required for $\text{C}_7\text{H}_6\text{IBr}$ .	Found.	
Carbon	28.28	27.66	...
Hydrogen	2.03	2.31	...
Iodine and Bromine	69.69	69.47	68.41
	<hr/> 100.00	<hr/> 99.44	

*Properties.*—Crystallized from alcohol it forms flattened

\* V. Meyer, Ber. d. chem. Gesell., 1875, p. 1074, note.

needles, which usually have a straw-yellow color, but can be obtained white by repeated recrystallization with bone-black. It has an aromatic odor, and attacks the mucous membrane much less violently than any of the other substances mentioned in this paper; this, however, is very probably due to the fact that it is not readily volatile at ordinary temperatures: it melts at  $78\frac{3}{4}^{\circ}$ ; does not distil with steam or only with great difficulty; sublimes in needles; burns with a luminous green-bordered flame; and is insoluble in water, almost so in cold, much more soluble in hot alcohol, but slightly soluble in glacial acetic acid, freely in ether, benzole, and carbonic disulphide. It is not easily attacked, if at all, by an oxidizing mixture of potassic dichromate and dilute sulphuric acid.

That all the substances mentioned in this paper contain bromine in the side-chain is proved by the fact that, when boiled with alcoholic sodic acetate, each one of them yields the corresponding substituted benzylacetate, from which the alcohol can be obtained by heating with aqueous ammonia at  $150^{\circ}$  to  $160^{\circ}$ . The description of these compounds, as well as of certain other derivatives of these substances, will be found in the following articles of this series.

In closing this paper I am very glad to have an opportunity of thanking Mr. A. W. Field for the intelligent and skillful assistance which he has given me in the preparation of these substances.

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## AN APPARATUS FOR GAS ANALYSIS FROM SIMPLE LABORATORY MATERIAL.

BY A. V. E. YOUNG,

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While working in the subject of gas analysis with the simple Bunsen apparatus, none of the more complicated forms being available, the desirability of effecting economy in time and labor, and of applying liquid reagents entirely outside of

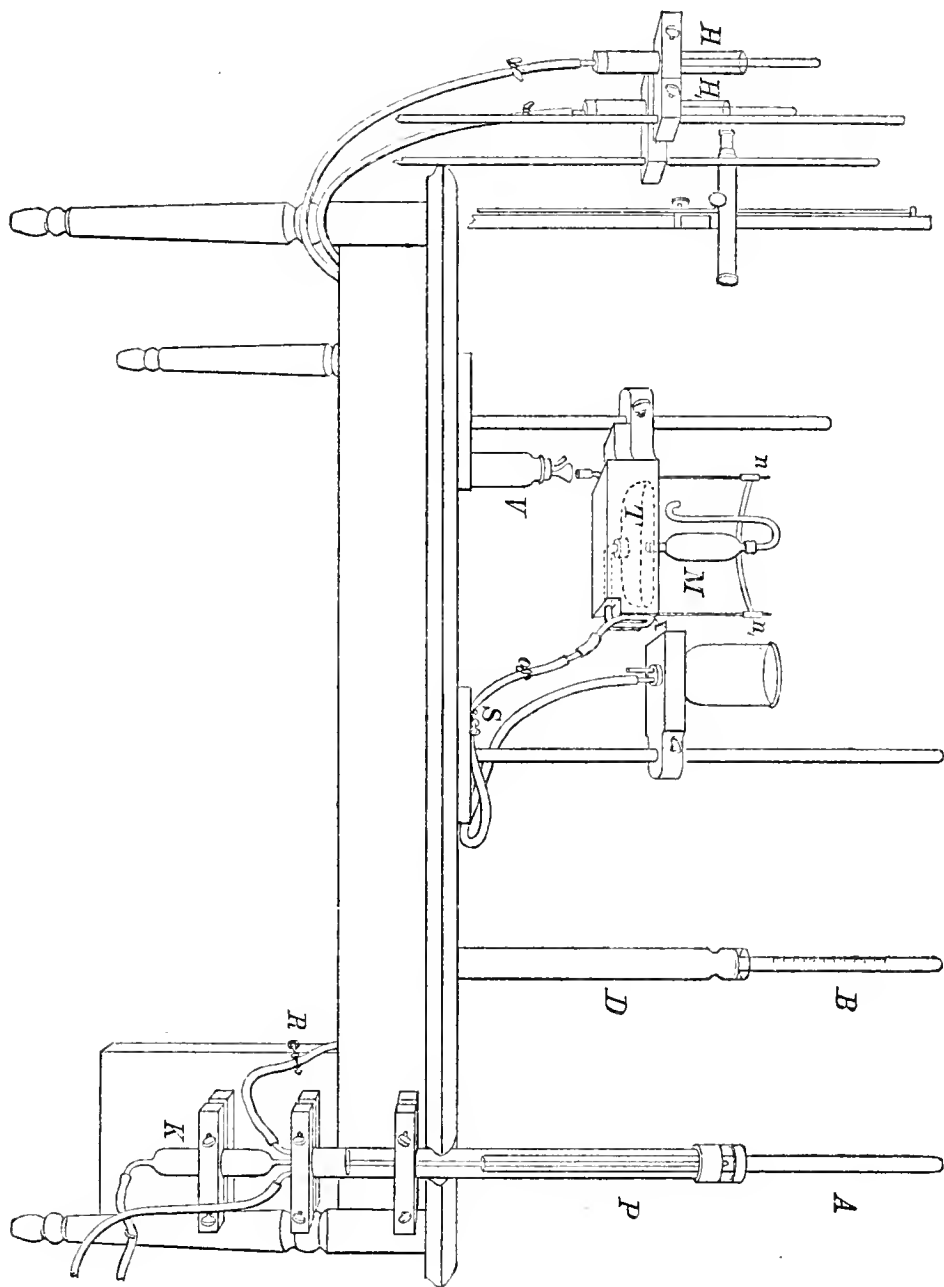
the measuring tube, led me to attempt to realize these results, so far as might be, by some additional apparatus of easy construction and demanding only such material as is usually at hand in a chemical laboratory, or at least easily obtainable. The apparatus thus designed, and now in satisfactory operation, may be described in three parts: 1. The measuring apparatus; 2. The transferring pipette; and 3. The absorption or laboratory vessel.

For the purposes of measurement and explosion the ordinary Bunsen's eudiometer is used, with the platinum wires and millimeter scale, and calibrated as described in Bunsen's "Gasometrische Methoden." To avoid the necessity of barometric and thermometric reductions, the principle of measurement by comparison with a standard volume of air, as described by Williamson and Russel\*, is used; but the means employed are different. Instead of raising and lowering the pressure-tube and eudiometer in the same mercury-trough, each tube is supported by an ordinary retort-stand in its own well and remains stationary, while the surface of the mercury is raised or lowered to bring the gases to the desired volume. For pressure-tube a second eudiometer (*B*, *Fig.*) is used. As cistern for this, a student-lamp chimney (*D*), closed at its smaller and lower end by a rubber stopper, serves very well. In order to raise or lower the surface of mercury a small glass tube passes through this stopper and through the top of the work-table, and connects by means of small rubber and glass tubing running underneath the table with a small cylinder and piston (*H*). The cylinder is made of a piece of glass tubing 120 mm. long and 33 mm. in diameter, closed at one end by a cork, through which passes the connecting tube. The piston consists of a cork on the end of a stout glass rod, and fits the cylinder with sufficient closeness to effect the depression and retention of the surface of mercury in the cylinder below the level of that in the cistern, which is in communication with it. The cylinder is supported in a common wooden clamp, which slides up and down upon a rod placed near the telescope, so that the piston can be conveniently raised or lowered by the right hand while the eye is at the telescope. The latter is placed at one end of the work-table

\* Proc. Roy. Soc. vol. ix. p. 218.

and the pressure-tube stands near the opposite end, the distance between them being about 2 meters.\*

To put in order the pressure-tube, the cistern, cylinder and connecting tubes are filled with mercury, care being taken



that no bubbles of air are retained. The pressure-tube is then partly filled, a convenient volume of air being retained, the

\*In the figure the pressure-tube *B* is somewhat displaced from its true position in order to bring it into clearer view. It should stand at the same distance from the telescope as the endiometer *A*.

saturation of which with aqueous vapor is insured by moistening the walls of the tube before filling. The tube is then inverted and transferred to the mouth of the cistern by means of the shallow spoon used for such purposes; then fixed in a retort-stand in such a position that the enclosed air has a convenient volume, say 300 on the millimeter scale, and the level of the mercury in the tube is from 30 to 60 mm. above that in the outer vessel. Now if the enclosed air undergoes change of volume, it is brought back to its initial volume by means of the piston while the top of the mercury column is watched through the telescope.

To effect the application of liquid reagents outside of the measuring tube, the gas is first withdrawn from the eudiometer by means of the transferring apparatus, which also serves as cistern for it in the operation of measuring. This is simply a stationary pipette (*P*), large enough to receive within itself the eudiometer. It is made of a piece of glass tubing 545 mm. long and 33 mm. diameter, to the end of which is attached, by means of rubber packing and sealing-wax, a short tube of larger diameter, in order merely to make a mouth large enough to receive the eudiometer with its transferring spoon. An argand chimney 50 mm. in diameter was used for this purpose, the two when joined making a cylinder 610 mm. long. The bottom of this is tightly and firmly closed by a rubber stopper, through which pass three small glass tubes (*a*, *b*, *c*). The stopper is forced as far as possible into the tube, and the latter then heated until the rubber softens and adheres closely to the glass. One of the three tubes mentioned (*b*) is 615 mm. long and about 3 mm. interior diameter. It passes through the cylinder, axially, to within 28 mm. of the mouth. It is slightly drawn out at its upper end and the end well rounded. The second tube (*a*) merely passes through the stopper, and makes connection by means of rubber and glass tubing with the cylinder and piston, *H*, similar to the one already described. The third tube, *c*, communicates by a rubber tube with a mercury reservoir (not shown in the figure). The reservoir is held in a wooden clamp which slides up and down upon a post rising from the floor close to the table. The long tube, *b*, is connected by means of a piece of rubber tube only just long

enough to hold a screw clip, with one end of a glass bulb, *K*, 140 mm. long, 38 mm. diameter, the other end of which communicates with a second and smaller mercury reservoir supported like the first. All the rubber tubing used in the apparatus is stout and thick walled, measuring 12 mm. external and 4 mm. internal diameter. For reservoirs, inverted bell-jars answer the purpose, or, still better for the larger one, a druggist's percolator. The connection between the long pipette tube and the bulb below must be made with sufficient care to prevent leakage of gas even under considerable pressure, and also to make a clear channel from which all of the gas shall be expelled by the rise of mercury. Screw clips are placed on the rubber connecting tubes. The figure makes the position and support of the pipette sufficiently clear.

To prepare it for use, mercury is poured into the reservoirs and carefully allowed to fill the rubber tubes so as to expel all the air from them; then, by raising the smaller reservoir, mercury rises in the bulb and long axial tube, completely filling them, and the screw clip at the bulb is then closed. The cylinder of the pipette is then filled from the larger reservoir until the mercury rises a few mm. above the end of the axial tube. The whole is now ready for use, either in the measurement or transference of a volume of gas. For the first operation the eudiometer containing the gas is transferred to the mouth of the pipette, and there is sustained by the left hand while the right controls the level of mercury in the pipette by movements of the reservoir. It is thus lowered over the end of the axial tube until the mercury column sustained within it, read upon its millimeter scale, is a little longer than that in the pressure-tube, the air in the latter being at the initial volume 300. In this position it is fixed perpendicularly in the retort-stand, the clip upon the tube leading to the reservoir is closed, and that (*R*) upon the tube leading to the piston is opened. Now taking position at the telescope, the column in the pressure-tube is brought accurately to the division 300, the reading in the outer vessel giving, say, 350, that is, a column 50 mm. long. A slight turn of the telescope brings the eudiometer into view. The column in this, being, as mentioned above, longer than that in the pressure-tube, is shortened by pressure upon the piston until

it too is 50 mm. long. Now take the reading at the top of the column, and reference to the table of capacity gives the proper volume, provided the two tubes are in the same condition of temperature and atmospheric pressure and the gas in each is saturated with aqueous vapor.

To secure the first two conditions the tubes are not surrounded with water as in many forms of apparatus; but the readings are so easily made, involving no reductions, that it is a simple matter to take a sufficient number to show when they become constant. Ten or fifteen minutes usually suffice for this, if in handling the eudiometer its direct contact with the hand be avoided as much as possible. The apparatus permits an easy adjustment of the mercury levels, since a very considerable movement of the pistons produces but a slight movement of the columns. The final adjustment should always be made by a depression of the piston, that is, by forcing up the mercury column in the tube so that the curve of the meniscus may be always the same.

To effect the transfer of gas from the eudiometer, free the latter from its stand and lower it until its top rests upon the end of the axial tube of the pipette. Then lower the small mercury reservoir and open the clip at the bulb. The mercury sinks in the axial tube, and the gas follows it into the bulb below; meanwhile the mercury rises in the eudiometer until it is completely filled, the last bubble of gas being detached from the platinum wires by jarring the tube against the wall of the pipette. The mercury then flows into the axial tube and the clip at the bulb is quickly closed. The eudiometer is now withdrawn completely filled with mercury, and set aside until again needed. The rest of the operation is simply the reversal of this. The vessel to receive the gas is filled with mercury, transferred to the pipette, lowered over the end of the axial tube, the small reservoir raised and the clip at the bulb slowly and carefully opened. The gas then passes back to the receiver, followed by the mercury. When this flows from the axial tube the bulb-clip is closed and the transfer completed.

Next comes the operation of absorption. For this purpose it was first thought to use a straight tube like the eudiometer, but this was not found practicable. A very convenient and

satisfactory absorption vessel, *M*, is made from a large test-tube, about 180 mm. long and 30 mm. in diameter, by drawing out its bottom to a tube and cutting off the end so as to give an orifice about 1 mm. in diameter, and also drawing together somewhat the open mouth of the test-tube until it becomes about 18 mm. in diameter, so that it can be contained in the transferring spoon used with the endiometer. To the small end is attached by a bit of rubber tubing 18 mm. long a delivery tube of about 3 mm. bore, which rises a few millimeters above the rubber joint, and then is bent so as to descend parallel and near to the sides of the test-tube to the level of its mouth, and then turns slightly upwards. The inside of the rubber tube making the joint is carefully coated with paraffin to protect it against the reagents, and the delivery-tube is thrust into it somewhat warm, so as to make a gas-tight and at the same time a smooth channel from which all the gas shall be expelled by the rise of mercury within. This furnishes an absorption vessel without the use of any stop-cock, not fragile, and, even if broken, very easily replaced. It is found convenient to have several on hand, varying somewhat in capacity, so as to economize the mercury required to fill them.

In order to manipulate the gas contained in the absorption vessel, a small mercury tank, *T*, is provided, made very simply from a block of wood, and arranged to slide up and down upon a rod as shown in the figure. Its inner dimensions are, length 120 mm., width 55 mm., depth 25 mm. Through its bottom is cut a hole 45 mm. in diameter, and into this from the inner side is firmly pressed a rubber stopper, *m*. This is also pierced by an opening of such diameter (15 mm.) that when the mouth of the absorption vessel is pressed down into it, a joint is made sufficiently close to hold mercury. The opening of the stopper is closed from below by the end of a piece of glass tubing which is attached to the bottom of the tank to prevent strain upon it.\* The other end of the glass tube leads by a rubber connection to a small reservoir, which like the others can be raised and lowered. The tank is fixed in a position about 225 mm. above the table, and the rubber tube descends from it to the table and passes under a short

\*A bend was made in the tube, as shown at *x*, but was found to be unnecessary.

iron rod at *S*, (a similar one is shown at *R*), hinged at one end so that the other end can be pressed down upon the tube as it lies on the table and thus instantly close it. The rubber stopper is covered by the mercury in the tank to the depth of about 15 mm., so that when the mouth of the absorption vessel is pressed down into its rubber socket, both it and the end of the delivery-tube are completely under mercury. If now the reservoir be raised above the level of the tank and clamped there, and the communicating tube be opened by raising the lever at *S*, the mercury rises in the absorption vessel to its top and then passes down the delivery-tube, thus completely filling the vessel. By allowing it to flow for a few seconds, and then lowering the reservoir and reversing the flow, one can assure himself that no bubbles of gas are retained. By the lever at *S*, the flow of mercury can be perfectly regulated or instantly arrested at any point in the absorption vessel, or even in its descent through the delivery-tube. The tank is provided with an overflow tube which leads to any convenient vessel, *V*; also with a little wire frame, sufficiently shown in the figure at *n* and *n*, for the purpose of holding the absorption vessel erect when filled with mercury.

The operation of absorption, then, would be as follows, supposing the gas already measured and drawn into the pipette bulb: Two absorption vessels having been filled as described, one is set aside; into the other is injected the proper reagent, its delivery-tube having been first closed with a little plug of wood to hold the mercury column in position. It is then transferred to the pipette and lowered over the end of the axial tube until it rests upon the shoulder formed where the pipette cylinder joins the wider tube which forms its mouth. The delivery-tube need not enter the pipette at all. The gas is then allowed to pass in from the bulb, one bubble at a time if so desired. As the mercury is displaced it leaves the wall of the absorption vessel moistened with the reagent, thus exposing a large surface to the gas. When all the gas has passed, and the mercury has flowed for a few seconds, the bulb-clip is closed, and the absorption vessel transferred back to its socket in the tank. Here, by shaking it from side to side, and by letting a stream of mercury flow in through the

delivery-tube, considerable agitation of the gas and reagent can be effected. To recover the gas from the reagent, the second absorption vessel is lowered over the delivery-tube of the first, and held by the left hand while the right regulates the flow of mercury from the reservoir. The gas is thus passed into the second vessel, leaving most of the reagent, perhaps all, in the first. It is hardly safe, however, to attempt to pass it directly from the first into the endiometer, unless the quantity of reagent used is very small. The second absorption vessel is then pressed into the socket, the filled eudiometer placed over its delivery-tube and the gas passed as before, now free from reagent and ready for measurement. If the mercury column in descending the delivery-tube of the second vessel still bears some of the reagent upon its surface, its motion is arrested at about the middle of the tube and the tube sharply tapped, when the liquid will be drawn up leaving the mercury clean. If a second reagent must be used to absorb vapors from the first, it is injected into the second vessel, and thus cannot interfere with the action of the absorbent proper.

This absorption vessel can also be conveniently employed as collecting vessel in the volumetric estimation of nitrogen and other gases, when separation of gas from liquid is to be accomplished. It is also applicable in the use of reagents which attack mercury, as in the processes described by Berthelot\* for the use of nitric acid and bromine to determine benzol vapors, &c. After the absorption is completed as there described, the gas is passed under water from the flask or tube where the reaction takes place to the absorption vessel, previously filled with water. This is then transferred to its socket, and the gas freed from water as already explained.

Although the description here given is of the apparatus actually in use, it will be seen that the latter readily admits of such modifications in dimensions and disposition of parts as surrounding circumstances may suggest.

As indicating the possibility of accurate work with the apparatus are given the following results of two successive determinations of the oxygen in air by absorption with potassic pyrogallate :

\* *Ann. Chim. Phys.* (5) xii.

	First.	Second.
Air taken	197.23	207.20
After absorption	156.07	164.04
Oxygen	<u>41.16</u>	<u>43.16</u>
Oxygen in 100 of air	...	20.87
“ “ “	...	20.83

Bunsen gives 20.86 per cent. obtained with the same reagent and his absorption balls. The analysis of air can be made in about three-quarters of an hour.

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## ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

### II.—ON THE OXIDATION OF XYLENESULPHAMIDES.

BY IRA REMSEN AND M. W. ILES.

(Continued from p. 51.)

#### *Orthocresole from Oxytoluic Acid.*

Oxytoluic acid was intimately mixed with quick-lime in the proportion of one part of the former to one and a half parts of the latter. The mixture was distilled and an oil passed over, the main portion of which boiled between 180–190°. It had the characteristic odor of phenoles, and was colored brownish red. It was treated with calcium chloride, and then cooled down by means of a freezing mixture of ice and salt. The entire mass solidified. At the time this experiment was performed orthocresole was known only as a liquid which would not solidify in a freezing mixture. We showed, however, that the cresole in our hands was really orthocresole, and hence we must have obtained it in purer condition than it had hitherto been obtained. Subsequently Tiemann and Schotten\* showed that pure orthocresole does solidify easily.

\* Ber. d. chem. Gesell., 11, 767.

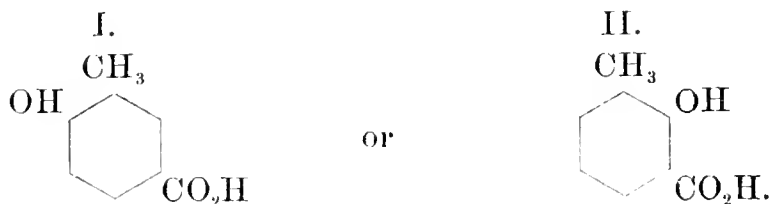
The cresole prepared in the experiment just described was treated with benzoylchloride, and the benzoyl-compound thus readily obtained. This made its appearance in the form of a light yellow oily liquid, which did not solidify in a freezing mixture. It corresponded closely in its properties to benzoyl-orthocresole described by Engelhardt and Latschinoff.\*

The most positive proof of the nature of this cresole was furnished by fusing it with potassium hydroxide. The substance was kept in contact with the fusing mass for about three hours, the temperature being kept comparatively low. At the end of this time, or when the oil drops had all disappeared, the whole was dissolved in water, acidified with hydrochloric acid and extracted with ether. The ethereal solution left behind, after evaporation, a white crystalline body. On crystallizing this body from water, long, delicate needles, resembling salicylic acid, were obtained in pure condition. The solution gave a violet color with ferric chloride. The substance was volatile with water vapor. The dried needles fused at  $154.5^{\circ}$ – $155^{\circ}$ . These properties suffice to show beyond a doubt that our product is salicylic acid. But not a trace of any other product could be found. Hence we are justified in concluding that the cresole obtained from our oxytoluic acid is pure ortho-cresole.

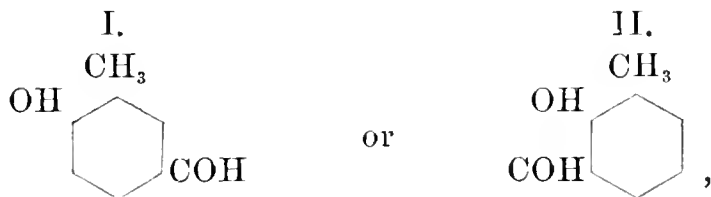
Another experiment was now performed, the result of which served to confirm the result of the experiment just described. A small quantity of the acid was heated in a sealed tube with concentrated hydrochloric acid at  $180^{\circ}$ – $185^{\circ}$  for about half an hour. The solution had a slightly reddish color, and a little free carbon was present. The acid solution was partially neutralized with caustic soda, and then extracted with ether. A reddish oil was obtained, and this fused with caustic potassa. In about two hours the operation was completed. On treating the mass in the usual manner a solid, white, crystallized body was obtained by evaporating the ethereal solution. This possessed all the properties of salicylic acid. It crystallized in long delicate needles from water. Its aqueous solution was colored violet by ferric chloride. It fused exactly at  $155^{\circ}$ . No other substance was formed, so that here again we have good grounds for concluding that the cresole obtained from the oxytoluic acid is only orthocresole.

\* Zeitschr. Chemie, N. F. 5, 621.

As the hydroxyl group is thus shown to be in the ortho-position with reference to the methyl-group in the oxytoluic acid, the latter may have one of two formulas. It may be either



Between these two formulas it would be impossible for us to decide without the aid of further experiments. These were performed and will be described below; but in the meantime an article by Tiemann and Schotten\* appeared, in which the same oxytoluic acid is described as that which we are considering. These chemists, however, obtained their acid in an entirely different way, and as they were led to accept the formula which we had already accepted, the probability of the correctness of the conclusion is doubly strong. Tiemann and Schotten started with orthocresole. On treating this with potassium hydroxide and chloroform, according to the now well-known reaction of Tiemann and Reimer, they obtained the aldehydes of two oxytoluic acids, one of which they call orthohomoparaoxybenzoic acid. They conclude that the formula of this acid is . The conclusion is based upon a large number of experiments performed by Tiemann and his associates which show that when the aldehyde group is introduced into a phenole, it takes either the para- or the ortho-position with reference to the hydroxyl. Accordingly an aldehyde obtained from ortho-cresole by this reaction would be either



but an acid corresponding to formula II. is already known,

\* Ber. d. chem. Gesell., 11, 767,

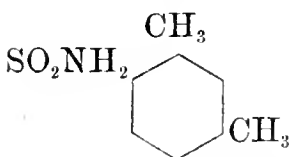
and this is not identical with orthohomoparaoxybenzoic acid. Hence formula I. must be the correct one.

The properties of orthohomoparaoxybenzoic acid agree in most respects with those of our oxytoluic acid; and though the account of the acid given by Tiemann and Schotten is very meagre, probably because it was obtained only in small quantity, still there seems to be no good ground to doubt that the two are identical. Their acid fuses at  $172^{\circ}$ – $173^{\circ}$ , after being dried at  $100^{\circ}$ . Under the same conditions our acid fuses at  $174^{\circ}$ – $175^{\circ}$  (corrected). Both acids contain half a molecule of water of crystallization. Both conduct themselves toward chloroform, alcohol, ether and water in the same way. Ferrie chloride colors neither one in aqueous solution. While our acid, however, crystallizes in long, delicate, lustrous needles of great beauty, orthohomoparaoxybenzoic acid is described as crystallizing "in kleinen, meist schwach fleischbroth gefärbten Nadeln." The difference is probably due to a difference in the degree of purity in which the two substances were prepared. Our acid was undoubtedly perfectly pure, while that of Tiemann and Schotten could not have been so.

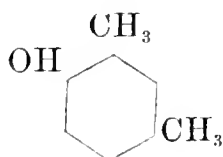
Again it is interesting to note that Jacobsen\* has succeeded in obtaining another oxytoluic acid from the same xylenesulphamide with which we started, *i. e.* the  $\alpha$ -amide of fusing point  $137^{\circ}$ . He fused the amide directly with potassium hydroxide, and thus obtained, as his first product, the corresponding xylenole. On then further fusing this xylenole with potassium hydroxide, it was first converted into an oxytoluic acid. This acid is not identical with ours, as Jacobsen's description plainly shows. It does not contain water of crystallization. It fuses at  $149^{\circ}$  (uncorr.). Its solution is colored deep violet by ferrie chloride. Its barium salt contains two molecules of water of crystallization, while that described by us contains three molecules of water. The copper salt could not be prepared in good condition, while the copper salt of our acid is very characteristic. The acid of Jacobsen further presents a peculiarity which ours does not present. When distilled with lime it yields orthocresole, as ours does; but when heated in a sealed tube with concentrated hydrochloric acid at  $180$ – $185^{\circ}$ , it is split up into carbon dioxide and *paracresole*. Our acid, as was

\* Ber. d. chem. Gesell., 11, 374.

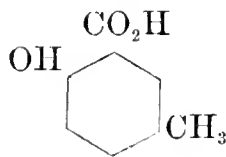
fully described above, yields orthocresole under the influence of both these reagents. Jacobsen regards the experiment with hydrochloric acid as reliable, and considers his acid a derivative of paraeresole. The transformations effected by Jacobsen may be represented thus :



Xylenesulphamide,  
fusing point 137.5°-138°.

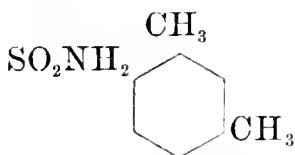


Metaxyleneol.

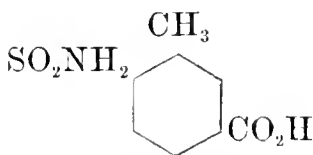


Oxytoluic acid.

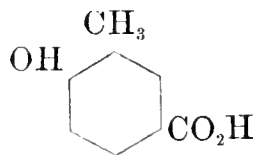
The transformations described by us may be represented thus :



Xylenesulphamide.

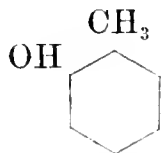


Sulphaminemetatoluic acid.

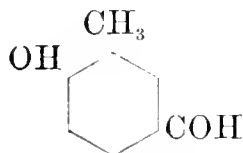


Oxytoluic acid.

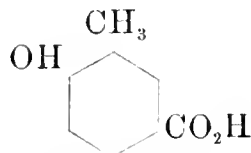
Finally, the transformations described by Tiemann and Schotten may be represented thus :



Orthocresole.



Orthohomoparaoxybenzaldehyde.



Orthohomoparaoxybenzoic acid.

We hope to be able to subject homoparaoxybenzoic acid to an exhaustive examination, as we can easily prepare it in large quantity.

It will be seen, on comparing Jacobsen's transformations with ours, that while the sulphamine group evidently protects the ortho-methyl group when the oxidation takes place in acid solution, the hydroxyl group does not protect the ortho-methyl group when the oxidation takes place in alkaline solution. On the contrary, in the latter case the ortho-methyl is first oxidized. Some other observations have been made since these experiments were performed which seem to indicate that it is a general principle, that when oxidation is effected

by means of fusing potassium hydroxide, the ortho-methyl is first oxidized. In another part of this memoir these relations will be considered more fully with reference to their bearing upon the structure of some mesitylene derivatives.

From a consideration then of the results of the experiments just described, we are led to the conclusion, that in our oxy-toluic acid the hydroxyl group occupies the ortho-position with reference to the methyl, and the para-position with reference to the carboxyl. Accordingly in sulphaminemetatoluic acid the sulphamine group probably occupies the same relative position. This, however, does not necessarily follow, as the transformations effected by means of fusing potassium hydroxide have, as is well known, been shown to be unreliable. It was hence considered necessary to furnish further proofs of the structure of the acid.

#### *Xylidinic Acid.*

If the sulphamine group in sulphaminemetatoluic acid could be converted into carboxyl, the product ought to be xylidinic acid, provided our notions concerning the structure of xylidinic acid and of the sulphamine acid are correct. As the sulphamine group can be so readily transformed into hydroxyl, it was thought that possibly the fusion of the sulphamine acid with sodium formate might also give good results.

Pure, dry potassium sulphaminemetatoluate was intimately mixed with an equal volume of sodium formate, and the mixture heated in a silver crucible. The fusion was performed at as low a temperature as possible. The phenomena which usually accompany this reaction were observed. The mass became black, and inflammable gases escaped from the mouth of the crucible, and these had the offensive odor characteristic of organic sulphur compounds. After cooling, the mass was dissolved in water, filtered, made ammoniacal and boiled with animal charcoal. Hydrochloric acid was added to the filtrate, and a precipitate with a yellow color obtained. This product was still quite impure. It was dissolved in a small quantity of alcohol, the solution filtered, and then a considerable quantity of water added. By repeating this process a few times a comparatively pure product was obtained, though it was found

to be very difficult to thoroughly purify the acid. It retained to the last a yellow tint. A small portion was sublimed, and was thus deposited in the form of short thick needles. These fused between  $280^{\circ}$ – $282.5^{\circ}$  (uncorr.). We examined a small specimen of xylidinic acid in our possession, and found that the two acids fused at exactly the same point. The acid obtained by us was extremely difficultly soluble in water, hot as well as cold. This fact also is in accordance with the supposition that we actually have to deal with xylidinic acid.

A portion of the acid was first neutralized with ammonia, and a solution of zinc sulphate added. On boiling this solution the highly characteristic *zinc salt* of xylidinic acid was thrown down, as described by Jacobsen.\* The salt was found to be very difficultly soluble in hot water, and comparatively easily in cold water.

The *calcium salt* was prepared by boiling the acid in water with finely powdered Iceland spar. It was obtained in the form of scales. Though recrystallized a number of times, the result of the analysis shows that it was not perfectly pure. Like the free acid, it retained a yellow color to the last.

0.2183 grams dried salt gave 0.1303 grams  $\text{CaSO}_4$ .

	Calculated.		Found.
$\text{C}_9\text{H}_6\text{O}_4$	178	...	...
Ca	40	18.35	17.55

Although the results of the experiment just described are not as satisfactory as could be desired, there can hardly be any doubt that the bibasic acid obtained was really xylidinic acid. Hence we are again led to the formula already accepted for sulphaminemetatoluic acid, and the conclusion drawn is made doubly probable. But the value of the reaction with sodium formate has been doubted as well as that with potassium hydroxide. Though the results reached through it could not then be considered decisive, any more than those reached through the reaction with potassium hydroxide, still when both lead to precisely the same conclusion it is plain that the chances are in favor of this conclusion being correct. We are, however, able to furnish still further proofs of its correctness.

\* Ber. d. chem. Gesell., 10, 859.

*Sulphoisophthalic Acid.*

The oxidizing mixtures from which the main portion of sulphaminemetatoluic acid was obtained were concentrated, and thus a few additional crops of crystals of the acid were obtained. In these new portions no second isomeric acid, except one derived from paraxylene, was discovered, though every precaution was taken against error. This fact again serves to strengthen the opinion expressed above that, if  $\beta$ -xylenesulphamide yields a monobasic acid by oxidation, this acid must be unstable towards the oxidizing mixture employed. Our object in examining the filtrates from the sulphaminemetatoluic acid first obtained was expressly to decide whether or not a second acid was formed. And, although the quantities worked up by us yielded nearly *eighty grams* of perfectly pure sulphaminemetatoluic acid, not an indication of the presence of an isomeric acid, except the one above referred to, was observed. At the same time two new products were obtained from the last mother-liquors, and these proved to be derivatives of bibasic acids.

Both the new products were found to be easily soluble in water, and to fuse at a much higher temperature than sulphaminemetatoluic acid. On purification they were found to crystallize well from water. A more careful examination showed them to be acid potassium salts. The quantities obtained from these mother-liquors were so small that it would have been impossible to determine the nature of the salts had we not soon discovered a method by which they could be prepared in large quantity and perfectly pure.

Suspecting that the salts might be derived from bibasic acids formed by further oxidation of the monobasic sulphaminemetatoluic acid and its isomere from paraxylene, and believing that the oxidation of the second methyl group could probably be more easily effected by means of potassium permanganate, an experiment was at once made with this agent. The result was perfectly satisfactory. It was found that sulphaminemetatoluic acid can be quantitatively converted into a new acid, and that the acid can be easily obtained in the form of its acid potassium salt. This salt is identical with one of those obtained, as above described, from the chromic acid oxi-

dizing mixtures. In the same way subsequent experiments showed that the second salt mentioned above could be readily formed by treating the monobasic acid derived from paraxylene with potassium permanganate. These derivatives from paraxylene will be considered farther on. At present we will confine our attention to the oxidation of sulphaminemetatoluic acid by means of potassium permanganate.

The best conditions for this experiment are, according to our experience, the following: To 1 gram sulphaminemetatoluic acid, take 5 grams potassium permanganate, and dissolve in 100 cc. water. This mixture is heated on a water-bath for about seven hours. At the end of this time a little permanganate still remains unreduced. A few drops of alcohol, or of a solution of sulphur dioxide, are added to effect the reduction, and, when the solution is colorless, it is filtered. The filtrate has a slightly alkaline reaction. It is evaporated down to about one-sixth to one-eighth of its volume, acidified with a little hydrochloric acid, and allowed to stand after filtering. On cooling, a perfectly homogeneous mass of acicular crystals is deposited. After one recrystallization these are, as far as could be determined, perfectly pure. On concentrating the mother-liquor from the first crop of crystals, a second deposit was obtained, and this, purified by recrystallization from water, proved to be identical with the first product. On still further concentrating, more of the substance crystallized out together with potassium chloride, but no other substance could be found. The conclusion is thus justified, that when sulphaminemetatoluic acid is treated with potassium permanganate, under the circumstances just described, it is completely converted into an acid which yields an acid potassium salt. The quantity of the salt obtained was, further, in accordance with this conclusion. The yield was almost quantitative. If any deep decomposition of the acid takes place it is to an exceedingly slight extent.

We naturally suspected that the new acid was sulphamine-isophthalic acid, produced by the oxidation of the second methyl group still contained in the monobasic acid, and the results of the determination of the amounts of potassium and sulphur contained in the salt confirmed this supposition. Nevertheless, on attempting to determine the amount of nitro-

gen in the salt we were surprised to find that none was present. On now testing for the presence of nitrogen by fusing a little of the salt with sodium and then testing for cyanogen, not a trace of nitrogen could be discovered. These tests were repeated very frequently, the greatest care being always taken, but the result was always the same. The oxidizing process has hence undoubtedly removed the nitrogen from the original substance. What acid could now have been formed from sulphaminemetatoluic acid containing no nitrogen but containing the same, or nearly the same, amount of potassium and of sulphur in its acid potassium salt? The molecular weight of sulphamineisophthalic acid is 245, while that of sulphoisophthalic acid is 246. A difference of only 1 in the molecular weights of substances as complex as these could not possibly be detected by means of our ordinary analyses. It, hence, seemed very probable that we had sulphoisophthalic acid before us, and this was afterwards shown to be the case. The results of the analyses of the potassium salt were as follows:

I. 0.257 grams salt lost 0.02875 grams  $\text{H}_2\text{O}$  at  $190^\circ$ ; and gave 0.07025 grams  $\text{K}_2\text{SO}_4$ .

II. 0.3461 grams salt lost 0.03925 grams  $\text{H}_2\text{O}$  at  $190^\circ$ ; and gave 0.0931 grams  $\text{K}_2\text{SO}_4$ .

III. 0.3931 grams salt lost 0.0446 grams  $\text{H}_2\text{O}$  at  $130^\circ$ ; and gave 0.1053 grams  $\text{K}_2\text{SO}_4$ .

IV. 0.340 grams salt gave 0.24222 grams  $\text{BaSO}_4$  when oxidized by fusion with caustic potassa and treatment with bromine water.

	Calculated.		Found.			
			I.	II.	III.	IV.
$\text{C}_8\text{H}_5\text{O}_7$	213	66.54	..	..	..	..
S	32	10.00	..	..	..	9.78
K	39.1	12.21	12.27	12.07	12.03	..
$2\text{H}_2\text{O}$	36	11.25	11.19	11.34	11.35	..
	<hr/>	<hr/>				
	320.1	100.00				

The salt is the *monopotassium salt of sulphoisophthalic acid*. While, from the absence of nitrogen, the substance can not, of course, be a derivative of sulphaminemetatoluic acid, it is interesting to notice how easily the results of the analyses of the

salts might deceive the experimenter in regard to the nature of the acid. It is a growing custom among chemists to rely upon determinations of the amount of metal and water of crystallization in a salt for information in regard to the composition of the acid. There are many cases, it is true, in which the complete analysis of salts seems to be superfluous. On the other hand, that there is danger in the usual method is indicated clearly by the example with which we are dealing; and it is certainly better to do some apparently superfluous work than to draw a radically wrong conclusion for want of this work. We speak feelingly upon this subject, for we were ourselves at first deceived; and, our erroneous impressions having been communicated in a short notice\* published in Germany a few month ago, Jacobsen was apparently misled by it; and, although we have corrected our first statement, Jacobsen still clings to the error with considerable tenacity. Indeed he goes so far as to assert† that “eine andere Säure (als die Sulfaminisophthalsäure) bildet sich ueberhaupt nicht bei der Oxydation des  $\alpha$ -Metaxylolsulfamids oder der zunächst daraus entstandenen Sulfamintoluylsäure.”

Whatever Jacobsen may have obtained in the course of his experiments by the oxidation of  $\alpha$ -xylenesulphamide, or of sulphaminemetatoluic acid, it is certain that his broad assertion is not true. It is difficult to understand why he should have obtained only one product, and we also only one, and the two should not be identical. As far as it is possible to judge from his descriptions of his experiments, we worked under essentially the same conditions. Nevertheless he asserts positively that his product is sulphamineisophthalic acid, and that no other product is formed. He gives an analysis which was made to determine the amount of nitrogen in his compound, and the results agree closely with those required by the formula.

In view of this very marked disagreement in our results, a very careful special series of experiments was undertaken by us to enable us to come to a final conclusion upon the subject. As the principal result, we may say here *that there can not be the slightest doubt that the substance obtained by us is in reality sulphisophthalic acid, and we have not succeeded in making sulphamineisophthalic acid up to the present.*

\* Ber. d. chem. Gesell., 11, 1326.

† Ibid. 11, 1529.

If the acid potassium salt obtained by us is a salt of sulphoisophthalic acid, then, as it contains but one atom of potassium in the molecule, there must still be two acid hydrogen atoms in each molecule of the salt. Whereas, plainly, if the salt is derived from sulphamineisophthalic acid, then there can only be one acid hydrogen atom in each molecule. Of course it is a very simple matter to decide between these two very different cases. It is only necessary to neutralize a weighed portion of the salt with a solution of an alkali of known strength. For this purpose a solution of ammonia ( $\frac{1}{10}$  normal) was used, and the results obtained are here detailed:

I. 0.1909 grams salt were titrated with the ammonia solution. There were used for neutralization 12 ccm., whereas 11.9 ccm. were required according to the theory.

II. 0.17975 grams salt required 11.3 ccm. of the solution of ammonia, while the theoretical amount is 11.2 ccm.

III. 0.8338 grams salt required 52 ccm. of the solution of ammonia, while the calculated quantity is 52.12 ccm.

These results permit only one conclusion. The acid from which the potassium salt is derived is *tribasic*; and, hence, can not be sulphamineisophthalic acid. Taking this fact together with those already stated, it is perfectly clear that our new acid can only be *sulphoisophthalic acid*.

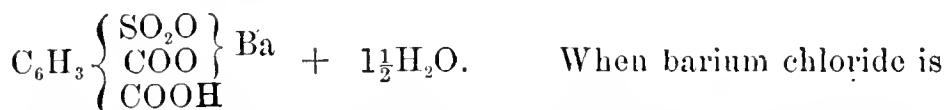
An objection might be made to our mode of experimenting. It might be thought possible that sulphamineisophthalic acid is actually formed at first, and that this is then converted into the sulpho-acid by evaporation in the alkaline solution. This seemed very improbable, as the solution was but very slightly alkaline. Then, too, Jacobsen worked just as we did, and yet, according to his statement, he obtained the sulphamine acid. Still we performed the experiment in such a way as to entirely meet the possible objection. Instead of adding the hydrochloric acid to the solution after evaporation, it was added immediately after the oxidation was finished, and the acid solution then evaporated. The product obtained contains no nitrogen, and is absolutely identical with the acid potassium salt already described.

If the attempt is made to explain the anomalies between the results obtained by Jacobsen and those obtained by us, embarrassment is the immediate result. It is very noteworthy that

the properties of the compound which Jacobsen considers to be sulphamineisophthalic acid, and of that one which, according to our experiments, is, beyond a doubt, sulphoisophthalic acid, are almost identical. They agree so closely that even Jacobsen assumes\* that we had the same acid that he had, and "allem Anscheine nach in reinem Zustande." In the description of the acid and its salts to be given below we shall call particular attention to these marked resemblances. Here it is sufficient to refer to the acid potassium salts of the two acids. The description given by Jacobsen for his acid potassium sulphamineisophthalate is almost word for word the same as our description of acid potassium sulphoisophthalate.

We have begun the study of sulphoisophthalic acid and its derivatives, and give here the results thus far reached.

*Monohydro-barium Sulphoisophthalate.*



added to a solution of the acid potassium salt, no change takes place in the cold. But on heating the solution a very difficultly soluble, crystalline barium salt is precipitated. As soon as it begins to appear, the contents of the vessel begin to bump so violently that they are thrown out, unless precautions are taken to prevent this result. This bumping is apparently characteristic of the barium salt; at least we have observed it in every preparation. The salt was collected, dried in the air and analyzed.

I. 0.2986 grams salt lost 0.0201 grams  $\text{H}_2\text{O}$  at  $200^\circ$ , and gave 0.16885 grams  $\text{BaSO}_4$ .

II. 0.21125 grams salt lost 0.0135 grams  $\text{H}_2\text{O}$  at  $210^\circ$ , and gave 0.1195 grams  $\text{BaSO}_4$ .

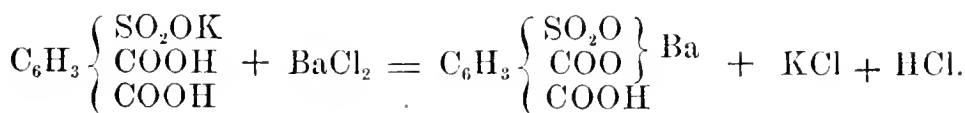
III. 0.2485 grams salt lost 0.01675 grams  $\text{H}_2\text{O}$  at  $210^\circ$ , and gave 0.141 grams  $\text{BaSO}_4$ .

IV. 0.2226 grams salt lost 0.0146 grams  $\text{H}_2\text{O}$  at  $210^\circ$ , and gave 0.1284 grams  $\text{BaSO}_4$ .

\* Ber. d. chem. Gesell., 11, 904.

	Calculated.		Found.			
			I.	II.	III.	IV.
$C_6H_4O_7S$	244	59.80	..	..	..	..
Ba	137	33.58	33.25	33.26	33.36	33.92
$1\frac{1}{2} H_2O$	27	6.62	6.73	6.39	6.74	6.56
	<hr/>	<hr/>				
	408	100.00				

The formation of the barium salt from the potassium salt takes place according to the equation :



Hydrochloric must be set free, if this equation expresses what takes place. In order to decide this point the solution from which the barium salt was precipitated was distilled, and the distillate examined for free hydrochloric acid. When the necessary concentration was reached, unmistakable evidence of the presence of the free acid in the distillate was obtained. The experiment was repeatedly performed, and always with the same result.

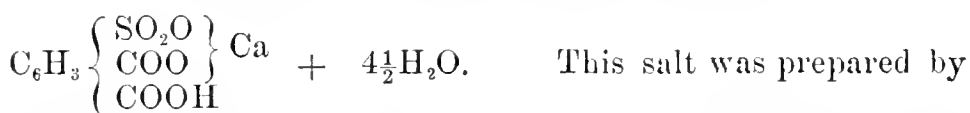
When this acid barium salt is treated with barium carbonate in water it passes into solution, and the process is accompanied by an evolution of carbon dioxide. This experiment again shows that the acid with which we are dealing is a tri-basic acid. The solution containing the neutral barium salt was evaporated, but it was soon seen that the salt was undergoing some decomposition. The liquid became cloudy, and a very difficultly soluble salt was deposited in crusts and as a fine powder. The character of this decomposition we have as yet been unable to investigate, but we hope soon to take up its study.

From the observations made by us we are inclined to the belief that the three acid groups contained in sulphisophthalic acid have different strengths. It is, of course, probable that the sulpho-group is stronger than the two carboxyl groups, but it also seems as though these two groups differ from each other. The observations bearing upon this point are as yet very imperfect, and they are only mentioned here to indicate a direction in which the study of this tribasic acid, as well as

another which has been prepared and is now being studied in this laboratory, will be taken up. If acetic acid is added to a solution of the neutral barium salt, the acid barium salt described above is precipitated, thus showing that acetic acid is stronger than one of the acid groups. If now hydrochloric acid be added to the difficultly soluble barium salt it is easily dissolved, showing that it is, at least partially, decomposed. It may be that the acid salt is completely decomposed by hydrochloric acid, yielding free sulphisophthalic acid, but in view of the great stability of the acid potassium salt, to be considered below, this does not seem probable. It hence appears that in sulphisophthalic acid one carboxyl is weaker than acetic acid, and one stronger, while they are both weaker than hydrochloric acid. It would, of course, be interesting to determine which of the carboxyl groups is the stronger, and attempts will be made to gain light upon this point. In general the study of the relations of different acid groups in the same molecule promises interesting results, and attention has already been turned to this field in our laboratory.

We have above called attention to the marked similarity between Jacobsen's description of the acid potassium salt of his sulphamineisophthalic acid and our description of the corresponding salt of sulphisophthalic acid. As regards the barium salt, Jacobsen says:\* "Aus der L sung (des sauren Kaliumsalzes) f llt Chlorbarium ein fast unl sliches, beim Kochen dichter und krystallinisch werdendes Bariumsalz." That is exactly what takes place in the case of sulphisophthalic acid. As Jacobsen gives no analyses of the salt prepared by him, a close comparison of the two is impossible.

*Monohydro-calcium Sulphisophthalate.*



treating the free acid with Iceland spar. It is probable that in the process of concentration, decomposition of the neutral salt first formed takes place, as noticed in the case of the neutral barium salt. The final solution, from which the salt

\* Ber. d. chem. Gesell., 11, 900.

here described was obtained, had been frequently filtered before it could be obtained clear. A closer study of the salt will show whether the supposition is correct. A somewhat similar case is presented by sulphoterephthalic acid, prepared and briefly described by Ascher.\* The salt obtained after treating the solution of the sulpho-acid with an excess of barium carbonate has the formula  $(C_6H_3 \{ \frac{(CO_2H)_2}{SO_3} \})_2 Ba$ .

The calcium salt under consideration is very easily soluble in water, and crystallizes in compact, apparently monoclinic prisms. The crystals lose part of their water of crystallization when exposed to the air.

The salt was analyzed with the following results:

I. 0.48475 grams salt lost 0.10875 grams  $H_2O$  at  $205^\circ$ , and gave 0.18225 grams  $CaSO_4$ .

II. 0.2223 grams salt lost 0.0490 grams  $H_2O$  at  $205^\circ$ , and gave 0.0840 grams  $CaSO_4$ .

	Calculated.		Found.	
			I.	II.
$C_8H_4O_7S$	244	66.85	...	...
Ca	40	10.96	11.06	11.11
$4\frac{1}{2}H_2O$	81	22.19	22.43	22.04
	<hr/>	<hr/>		
	365	100.00		

The *silver salt*, obtained by adding silver nitrate to a solution of one of the neutral salts, is amorphous, and difficultly soluble in water.

Finally, free sulphisophthalic acid was obtained by treating the acid barium salt with moderately concentrated sulphuric acid. The acid potassium salt is remarkably stable. It can be boiled with strong hydrochloric or sulphuric acid without undergoing decomposition, the salt crystallizing out of the acids on cooling. The free acid, obtained from the barium salt, is easily soluble in water, and crystallizes out of the concentrated solution in the form of short, lustrous needles. It fuses, according to our latest determinations with pure acid, at  $285^\circ$ – $287^\circ$ . In our first notice concerning this acid we gave the fusing-point  $282^\circ$ – $284^\circ$ . Now this is the point afterwards

\*Ann. der Chemie, 161, 3.

given by Jacobsen as that at which his sulphamineisophthalic acid fuses, so that here again we have a marked agreement in properties between two substances which are quite unlike in composition. We shall continue the study of sulphisophthalic acid, and shall hope to hear more concerning sulphamineisophthalic acid from Jacobsen, so that the differences between the two acids may become apparent.

The formation of sulphisophthalic acid by the action of the chromic acid mixture upon  $\alpha$ -xylenesulphamide is the first case in which the conversion of an ortho-methyl-group into carboxyl has been effected by the acid oxidizing agent. While this change plainly can be effected, contrary to the usually accepted notions on this subject, it is a significant and important fact that only a very small portion of the bibasic acid is formed, and the oxidation process which produces it must be regarded as altogether secondary to the main reaction. If this action were not secondary, if there were no conditions tending to prevent it, then, with an excess of the oxidizing mixture such as we employed, and long-continued heating, the monobasic acid must inevitably have disappeared, and the main product at least must have been the bibasic acid. But it has been shown that the amount of the monobasic acid obtained was very large, while that of the bibasic acid was comparatively insignificant. Hence it can not be doubted that something exerts a protective influence upon one of the methyl groups, and this we believe to be the negative group which is situated in the ortho-position with reference to the protected methyl. The fact that the protection is not complete is no objection to the view that protection is exerted; nor does it in the least detract from the importance of the general conclusion drawn in regard to the action of negative groups upon hydrocarbon residues in the ortho-position.

The transformation of the sulphamide-group into the sulpho-group by both the oxidizing agents used — chromic acid and potassium permanganate — is curious, and was entirely unexpected. From experiments since made here, it is certain that potassium permanganate does not effect this transformation of the sulphamide-group in all compounds; that in some cases the transformation is complete, while in still others it is only partial. Of course it is too early to offer anything like a final

opinion upon this new set of changes, but from the observations already made it seems probable that only those sulphamide-groups which are situated in the ortho-position with reference to groups undergoing oxidation are changed to the sulpho-group by oxidation. Three well-marked cases have been studied here thus far, and others will soon be taken up, but the consideration of this subject will be postponed until the investigations bearing upon it have been completed, or so far completed as to leave no doubt in regard to the interpretation to be offered.

*Transformation of Sulphoisophthalic Acid into Oxyisophthalic Acid ( $\alpha$ -Phenoledicarbonic Acid).*

The formation of sulphoisophthalic acid by the methods described above does not afford any aid in the solution of the main problem before us, which is the determination of the relative positions of the groups in sulphaminemetatoluic acid. While the experiments thus far discussed make it almost certain that the structure assigned by us to the compound is correct, there remains still another transformation to be described which only serves to confirm the conclusions already drawn. This is the transformation of sulphoisophthalic acid into the corresponding oxy-acid, which proved to be identical with  $\alpha$ -phenoledicarbonic acid, first prepared by Ost,\* and recently again by Tiemann and Reimer.†

Acid potassium sulphoisophthalate in moist condition was added gradually to fusing potassium hydroxide. The reaction proceeded quietly, and in a few minutes the change was complete. The mass was dissolved in water and hydrochloric acid added in excess. A voluminous precipitate was formed. This was colorless and consisted of very fine short needles. It was recrystallized from water, and, after the first crystallization, it was obtained in perfectly pure, white, delicate, short needles. The yield seemed to be quantitative. After drying, the acid was analyzed :

0.205 grams acid gave 0.064 grams  $H_2O$ , and 0.3952 grams  $CO_2$ .

\* Journ. prak. Chemie, N. F. 14, 93, and 15, 301.

† Ber. d. chem. Gesell., 10, 1571.

		Calculated.		Found.
C <sub>8</sub>	...	96	52.75	52.58
H <sub>6</sub>	...	6	3.30	3.47
O <sub>5</sub>	...	80	43.95	...
		182	100.00	

The analysis shows that the acid has the composition of an oxyphthalic acid.

The aqueous solution of the new acid is colored deep reddish violet by ferric chloride. It is very difficultly soluble in hot water, almost insoluble in cold water; easily soluble in alcohol and ether, insoluble in chloroform, even at the boiling temperature. The acid contains no water of crystallization, and fuses at 298–299° (uncorr.).

But these are the properties given by Ost and by Tiemann and Reimer as characterizing their  $\alpha$ -phenoledicarboxylic acid. The study of the salts of our acid also showed almost perfect agreement with the descriptions given for the salts of  $\alpha$ -phenoledicarboxylic acid.

*Barium oxyisophthalate*, C<sub>6</sub>H<sub>3</sub>.OH.(CO<sub>2</sub>)<sub>2</sub>Ba. This salt was made by treating the free acid with pure barium carbonate. It crystallizes in small, compact, radiating needles. It is easily soluble in hot and cold water. The dried salt was analyzed:

I. 0.1515 grams salt gave 0.11075 grams BaSO<sub>4</sub>.

II. 0.131 grams salt gave 0.0968 grams BaSO<sub>4</sub>.

		Calculated.		Found.	
				I.	II.
C <sub>8</sub> H <sub>4</sub> O <sub>5</sub>	...	180	56.79	...	...
Ba	...	137	43.21	42.98	43.45
		317	100.00		

*Calcium oxyisophthalate*, C<sub>6</sub>H<sub>3</sub>.OH.(CO<sub>2</sub>)<sub>2</sub>Ca, was prepared by treating the free acid with finely powdered Iceland spar. It crystallizes in small compact needles, very similar to those of the barium salt, and is, like the barium salt, easily soluble in cold and hot water. The dried salt was analyzed:

I. 0.1147 grams salt gave 0.070 grams CaSO<sub>4</sub>.

II. 0.07775 grams salt gave 0.0475 grams CaSO<sub>4</sub>.

		Calculated.		Found.	
				I.	II.
$C_8H_4O_5$	...	180	81.82	...	...
Ca	...	40	18.18	17.95	17.97
		220	100.00		

*Cadmium oxyisophthalate*,  $C_6H_3.OH(CO_2)_2 Cd$ . This salt was prepared by adding cadmium nitrate to a solution of the neutral ammonium salt. After a short time it separates in fine, short needles. Its properties agree with those given by Ost. It was analyzed after being allowed to dry in the air:

I. 0.22925 grams salt lost 0.05825 grams  $H_2O$  at  $160^\circ$ .

II. 0.25275 grams salt lost 0.0645 grams  $H_2O$  at  $160^\circ$ , and gave 0.08325 grams  $CdO$ .

		Calculated.		Found.	
				I.	II.
$C_8H_4O_5$	...	180	46.04	...	...
Cd	...	112	28.64	...	28.83
$5\frac{1}{2}H_2O$	...	99	25.32	25.41	25.52
		391	100.00		

*Normal silver salt*,  $C_6H_3.OH \begin{smallmatrix} CO_2Ag \\ CO_2Ag \end{smallmatrix}$ . This was obtained as an amorphous precipitate on adding silver nitrate to a solution of the neutral ammonium salt. Its properties agreed with those given by Ost for his neutral silver salt. Like the latter, our salt held a small amount of moisture very firmly, and, in order to get it perfectly dry, we heated up to  $180^\circ$  for some time. It contains no water of crystallization.

0.26465 grams salt gave 0.14475 grams Ag.

		Calculated.		Found.
$C_8H_4O_5$	...	180	45.45	...
$Ag_2$	...	216	54.55	54.69
		396	100.00	

*Acid silver salt*,  $C_6H_3.OH \begin{smallmatrix} CO_2H \\ CO_2Ag \end{smallmatrix}$ . According to Ost, if an excess of silver nitrate is added to a solution of free oxyisophthalic acid, the acid silver salt is formed, and separates in the

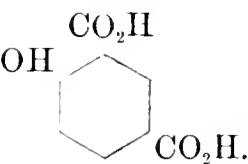
form of fine needles. We cannot confirm this statement. The experiment was performed repeatedly, and the neutral silver salt obtained in each case. In some experiments the amount of silver contained in the salt obtained was a little less than that required by the neutral salt, but it was never nearly as small as that required for the acid salt. If, on the other hand, acetic acid be added to the solution of the neutral ammonium salt, as recommended by Tiemann and Reimer,\* and then an excess of silver nitrate added, the acid silver salt separates readily, and possesses the properties mentioned by Ost and by Tiemann and Reimer. In view of the fact that all other salts of our acid agree closely with the same salts of  $\alpha$ -phenoledicarboxylic acid, it seems at least possible that Ost's observation with reference to the formation of the acid silver salt is not correct. Perhaps his solution of silver nitrate contained a little free nitric acid.

The analysis of the acid silver salt gave the following result:

0.41 grams salt gave 0.1525 grams Ag.

		Calculated.		Found.
$C_8H_5O_5$	...	181	62.63	...
$\frac{1}{2}Ag$	...	108	37.37	37.20
		289	100.00	

The salt crystallizes in fine needles, which are very difficultly soluble in cold water, and easily soluble in hot water. Further, we applied all the tests which are given by Tiemann and Reimer,† and were unable to detect any difference between our acid and  $\alpha$ -phenoledicarboxylic acid. There can hence be no doubt that our product is the latter acid.

If our views in regard to the structure of sulphaminemetatoluic acid are correct,  $\alpha$ -phenoledicarboxylic acid ought to have one carboxyl group in the ortho-position and the other in the para-position with hydroxyl group. Its formula may be conveniently represented thus,  reference to the formula may be convenient. But this is the formula by Tiemann and Reimer, and they were led to it by entirely differ-

\* Ber. d. chem. Gesell., 10, 1574, Tab. II.

† Loc. cit. p. 1574, Tab. II.

ent lines of thought. It is unnecessary to recapitulate here in detail the arguments of these chemists in favor of the formula given, but it may be mentioned that Ost succeeded in obtaining from his acid both salicylic and paraoxybenzoic acids. This indicates that the hydroxyl occupies the positions with reference to the two carboxyls which are characteristic of salicylic and paraoxybenzoic acids. And again Tiemann and Reimer made  $\alpha$ -phenoledicarboxylic acid by introducing a carboxyl group into salicylic acid, and also by introducing a carboxyl group into paraoxybenzoic acid, and the conclusion is again forced upon us that in the bibasic acid we have, as it were, a combination of salicylic and paraoxybenzoic acids, a fact which is expressed very clearly by the formula above given.

#### Conclusion.

Thus our first conception in regard to the nature of sulphaminemetatoluic acid is shown to be correct by a variety of methods of proof; and up to the present not a single fact is known to us which is not in perfect harmony with the conception.

Jacobsen has given other proofs for the structure of the  $\alpha$ -xylenesulphamide with which we started, and the results of his experiments agree with those performed by us, as far as they bear upon the structure of the amide. His method of work was entirely different from ours. He first converted the amide into the corresponding sulphonic acid, and fused the potassium salt of the acid with potassium cyanide. The cyanide thus obtained was heated with concentrated hydrochloric acid at  $180^{\circ}$ . Thus an acid was formed which was volatile with water vapor. Another portion of the potassium salt used in the experiment just mentioned was fused with sodium formate, and an acid produced which proved to be identical with the one from the cyanide. The acid thus obtained is xylylic acid. It was further oxidized by means of potassium permanganate yielding xylidinic acid. This transformation shows that  $\alpha$ -metaxylenesulphamide has the structure which we have already assigned to it on the basis of our experiments.

We have thus proved satisfactorily that when a substance

in which there are present a sulphamide-group and two methyl-groups, the former being in the ortho-position with reference to one methyl and in the para-position with reference to the other methyl, is oxidized by means of potassium pyrochromate and sulphuric acid, the ortho-methyl is almost completely protected from the action of the oxidizing agent, while the para-methyl is easily converted into carboxyl. One step has been taken towards showing what antecedent conditions are common in connection with the phenomena briefly discussed in the introduction to this memoir. But of course it is necessary to show that negative groups in other cases protect hydrocarbon residues in the ortho-position. Since these investigations were begun, some experiments have been performed by other chemists, the results of which are in accordance with our hypothesis; and, though one of us (R) will have occasion to discuss these results hereafter, it may be well at least briefly to refer to them at this point, as they are of the highest importance for us.

E. v. Gerichten has shown\* very recently that when a chloreymene, derived from carvacrole, is oxidized, it yields a chlortoluic acid. Now, in the chloreymene employed it is known that the chlorine occupies the ortho-position with reference to the methyl, and the meta-position with reference to the propyl. But the propyl group is converted into carboxyl by oxidation, while the methyl is protected—a result which, as will be seen, serves to confirm the hypothesis. Again the same chemist has made an isomeric chloreymene from thymole, and in this derivative the chlorine occupies the ortho-position with reference to the propyl, and the meta-position with reference to the methyl. On oxidizing this an acid was formed which has the composition of a chlorpropylbenzoic acid. The natural conclusion was that now the propyl had been protected while the methyl had been changed to carboxyl. This should certainly be the true explanation if our hypothesis is correct. In a later publication,† however, v. Gerichten claims that the acid formed by oxidation of the chloreymene from thymole is not a chlorpropylbenzoic acid, but that it has the composition  $C_6H_3.CH_3.Cl.C_2H_4.CO_2H$ , according to which it is methylchlorhydrocinnamic acid. If this is true, then, as v.

Gerichten says, the protection exerted upon the propyl-group by the chlorine in the ortho-position is not complete but only partial. It would, however, be very remarkable to find that a methyl-group in a compound like the chloreymene of v. Gerichten should resist the action of chromic acid. It will be shown in the course of these investigations that orthomethyl groups, situated exactly like this remarkable one in the molecule, are oxidized with great ease; and, indeed, the experiment of v. Gerichten upon the other chloreymene shows that a hydrocarbon residue situated in the meta-position with reference to the negative group can be oxidized. Why then, we repeat, should this solitary methyl act so strangely? As v. Gerichten still entertains some doubt concerning the correctness of his conclusion in regard to his last experiment, it may, perhaps, not be going too far if we also reserve our opinion until something more definite is heard about the new methyl-chlorhydrocinnamic acid. It is possible that it may finally prove to be what it was originally thought to be, viz. chlorpropylbenzoic acid.

Again, Schmitz has just published\* the results of an investigation on mesitylene derivatives, and some of these results bear closely upon the question we are discussing. He examines the nitromesitylenic acid formed by oxidation of nitromesitylene, and finds that in it the nitro-group is situated in the ortho-position with reference to both the methyl-groups; a fact which shows that the negative group exerts a protecting influence upon both these methyl-groups. The same fact was proved in connection with brommesitylenic acid obtained by oxidation of brommesitylene; the bromine protects two of the methyl-groups, and the third, being unprotected, is oxidized.

In the parts of these investigations which are still to be presented, other cases similar to the one we have thus far been chiefly occupied with will be considered. In the first portion of this paper we referred to an amide obtained by us from the first crude mixture which we suspected to be a derivative of paraxylene. This was deposited from the last mother-liquors in the form of verrucous masses, and found to fuse at 143°. In order to determine its nature it was first subjected to oxi-

\*Ann. der Chemie, 193, 160.

dation and converted into a monobasic acid. This acid, on being heated with concentrated hydrochloric acid up to  $220^{\circ}$ , was converted into a new substance which crystallized from the liquid on cooling. The crystals were filtered off and recrystallized, and, after drying, they were sublimed. They then fused at  $174^{\circ}$ . Although paratoluic acid, when perfectly pure, melts at  $178^{\circ}$ , still the properties of this substance are such as to leave little doubt that it is paratoluic acid. A small quantity of the supposed paratoluic acid was treated with potassium pyrochromate and sulphuric acid. It was thus converted into an acid which is insoluble in water, and did not fuse at  $310^{\circ}$ . This, in all probability, is terephthalic acid.

We hence conclude that the acid derived from the amide is sulphamineparatoluic acid, and further that the amide is a derivative of paraxylene as we supposed. We prepared more of the new acid and studied some of its salts, but it still remains to decide positively what relation exists between the three groups in the compound. It will probably be shown that the sulphamide group occupies the meta-position with reference to the carboxyl, and the ortho-position with reference to the methyl. The account of the full investigation of this acid will be given later. A method has been discovered by which it can be prepared in almost unlimited quantity, so that the investigation of its relations will be somewhat exhaustive.

Further, we have shown that sulphamineparatoluic acid is converted by oxidation with potassium permanganate into a tribasic acid very similar to sulphoisophthalic acid. This, in all probability, is sulphoterephthalic acid, as it is tribasic and contains no nitrogen. It can be obtained in any desired quantity and will be subjected to careful study.\*

### III.—ON THE OXIDATION OF BROMPARAETHYLTOLUENE.

BY IRA REMSEN AND H. N. MORSE.

If the hypothesis in regard to the protective influence exerted by negative groups upon hydrocarbon residues in the ortho-position were firmly established, it is plain that it might

\*Dr. L. B. Hall is engaged in the thorough investigation of the compounds here mentioned as derived from paraxylene. Instead of starting from paraxylene, however, he makes use of cymene, and obtains the same products.

be made use of for the purpose of determining the structure of some compounds at present not understood. Suppose, for example, we introduce into any aromatic hydrocarbon containing two residues some negative group, and then subject the product to the action of potassium pyrochromate and sulphuric acid. *If a stable monobasic acid is produced*, then the negative group occupies the ortho-position with reference to the residue which remains unchanged. While it would be premature to state that the hypothesis upon which this method of proof is based is firmly established, it seems extremely probable that the statement may soon be made with confidence. In the meantime we have performed the experiments to be described in this article, leaving for further investigations to decide whether the arguments employed are valid or not. Whatever may be the ultimate fate of the hypothesis, however, the facts embodied in this description will of course remain facts, though the interpretation of them may be found to be incorrect.

Within the past few years a great many experiments have been performed with the object of determining the influence which one substituting group exerts upon a second or third entering the same benzene-nucleus. These experiments have been confined to cases in which the most common substituting groups or atoms, as Cl, Br, NO<sub>2</sub>, SO<sub>3</sub>H, etc., were studied with reference to their influence upon one another, or with reference to the influence exerted upon them by such groups as hydrocarbon residues, or by CO<sub>2</sub>H, CH<sub>2</sub>OH, NH<sub>2</sub>, etc. Interesting generalizations have been reached. It is now known that all the so-called negative groups are influenced in essentially the same way by hydrocarbon residues, by carboxyl, etc. But while it has been recognized that the influence of all hydrocarbon residues is the *same in kind*, the question whether there is any recognizable *difference in degree* between the influence exerted by the group CH<sub>3</sub>, and that exerted by C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, etc., has never, we believe, been the subject of definite experimental inquiry.

There are, indeed, experiments on record which bear directly upon the question, but their connection with the question has not been pointed out; and it is fair to presume that it has not been recognized. We have hence undertaken the study of the subject here suggested.

Two methods of investigation might, theoretically at least, lead to the desired results. In the first place, substituting agents might be allowed to act upon analogous compounds, one of which contains the group  $\text{CH}_3$ , the other  $\text{C}_2\text{H}_5$ . Thus, for instance, the action of bromine, sulphuric acid, etc., upon toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ , might be compared with their action upon ethylbenzene,  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ . It is probable that in the latter case, as in the former, we would obtain mainly derivatives belonging to the para-series, together with smaller quantities of the isomeric ortho-products; but the proportions between the two isomeric products might be different in the two cases. To take a particular case, the definite question to be answered would be: Is the relation between the quantities of the para- and the ortho-derivatives the same when bromine acts upon ethylbenzene as when it acts upon toluene?

The difficulty which first presents itself in connection with this method of investigation consists in the fact, that the relation between the quantities of para- and ortho-derivatives formed from toluene itself and any given substituting agent is by no means constant, but dependent upon circumstances. Not only so, but the circumstances which determine the relation in any case are for the most part unknown to us, and are hence not under our control. Results obtained in the manner indicated could not then at present be reliable.

In the second place, some compound might be taken in which two different hydrocarbon residues are present, and the products derived from it compared with those obtained from an analogous substance which contains only one kind of hydrocarbon residue. Thus, as a convenient example for study, we may take the ethyltoluene of the para-series. The analogous compound, paraxylene, is well known, and the action of substituting agents upon it has been the subject of careful study. All known facts justify the assumption that only one mono-substitution product can be obtained from paraxylene with any one substituting agent. It is very likely that in a compound with a symmetrical structure, as that of paraxylene is supposed to be, the substitution takes place in connection with any one of the hydrogen atoms. Which atom is actually replaced at any given instant depends merely upon which part of the molecule is first presented to the agent. In

ethyltoluene, however, there are two kinds of replaceable hydrogen-atoms, and the action of a substituting agent upon this compound may give rise to three different results, according to the way in which the groups  $C_2H_5$  and  $CH_3$  act upon the entering atom or group. These possible results are:

1st. The formation of a product in which the substituting group occupies the ortho-position with reference to the  $CH_3$ , and the meta-position with reference to the  $C_2H_5$ .

2d. The formation of an isomeric product, in which the substituting group occupies the ortho-position with reference to the  $C_2H_5$ , and the meta-position with reference to the  $CH_3$ .

3d. The formation of both isomeric products in various proportions.

If the two hydrocarbon residues act with the same, or nearly the same, intensity upon the entering group, it seems clear that the third result ought to follow, *i. e.* both possible isomeric products should be formed in equal or nearly equal quantities, while the formation of only one product would indicate pretty positively that one of the groups  $CH_3$  or  $C_2H_5$  acts more strongly than the other. According to our experiments the result actually obtained is the first of the three mentioned. The product formed by allowing bromine to act upon ethyltoluene is, we believe, that in which bromine stands in the ortho-relation to the methyl, and the meta-relation to the ethyl.

Ethyltoluene was made according to the usual method, by treating a mixture of ethyl iodide and parabromtoluene in anhydrous ether with sodium. The parabromtoluene was a perfectly pure substance which boiled at a constant temperature, and crystallized on cooling so as to form a thoroughly solid mass. The action was moderated by cooling with ice water. An evolution of gas continued for more than twenty-four hours. When the reaction was finished the mass was distilled and the collected oil subjected to fractional distillation. It consisted of considerable benzene, toluene and ditolyl, together with the desired ethyltoluene which boiled at  $158^\circ$ – $160^\circ$ . The reaction was quite unsatisfactory and the yield small, although great care was taken to insure absolute purity of the materials employed.

Those portions of the distillate which boiled between  $155^\circ$

and  $165^{\circ}$  were treated in a small flask surrounded by cold water, with somewhat less than the theoretical quantity of bromine. When the reaction, which was rapid though not violent, was finished, the product was heated to drive off hydrobromic acid and the excess of bromine, and then distilled until decomposition began.

The bromine product thus obtained was treated with the usual oxidizing mixture of potassium pyrochromate, sulphuric acid and water. The mixture was gently heated for about twenty-four hours. At the end of this time the bromine product had disappeared, while the oxidation-product was present in the form of irregular lumps upon the bottom of the flask. These lumps were filtered off, washed with water, boiled with dilute sodium carbonate, the solution filtered and the acid precipitated by means of hydrochloric acid.

After filtering and washing the acid, it was converted into the barium salt by boiling it in water with pure barium carbonate. The solution of the barium salt was boiled with animal charcoal to remove a slight yellow color. After recrystallizing the salt a few times, it presented all the properties mentioned by Jannasch and Dieckmann\* as characterizing the barium salt of bromparatoluic acid.

It was analyzed with the following results:

I. 0.1518 grams salt lost 0.0169 grams  $\text{H}_2\text{O}$  at  $110^{\circ}$ .

II. 0.1846 grams salt gave 0.06617 grams  $\text{BaSO}_4$ .

III. 0.1001 grams salt lost 0.0114 grams  $\text{H}_2\text{O}$  at  $180^{\circ}$ , and gave 0.036 grams  $\text{BaSO}_4$ .

		Calculated.		Found.		
				I.	II.	III.
$(\text{C}_8\text{H}_6\text{BrO}_2)_2$	...	428	67.20	...	...	...
Ba	...	137	21.50	...	21.10	21.10
$4\text{H}_2\text{O}$	...	72	11.30	11.10	...	11.37
		637	100.00			

The formula of the salt is thus seen to be  $(\text{C}_6\text{H}_3\text{Br}.\text{CH}_3.\text{CO}_2)_2$  Ba +  $4\text{H}_2\text{O}$ , and this is also the formula of the known barium salt of bromparatoluic acid.

\*Ann. der Chemie, 171, 84.

The calcium salt of the acid was made by boiling some of the acid recovered from the purified barium salt with pure calcium carbonate. It is only necessary to say that the salt proved to be in every respect identical with that described in the paper by Jannasch and Dieckmann referred to above. Its analysis yielded the following results:

0.2597 grams salt lost 0.0277 grams  $\text{H}_2\text{O}$  at  $180^\circ$ , and gave 0.0668 grams  $\text{CaSO}_4$ .

		Calculated.		Found.
$(\text{C}_8\text{H}_6\text{BrO}_2)_2$	...	428	81.67	...
Ca	...	40	7.66	7.55
$3\text{H}_2\text{O}$	...	54	10.67	10.37
		<hr/> 522	<hr/> 100.00	

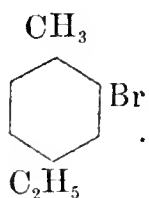
Further, the free acid possessed all the properties attributed to it by those who have previously described it. Its melting point was found to be  $203^\circ$ – $204^\circ$ .

Finally, the acid was treated with sodium amalgam for some hours. The bromine was thus extracted, and an acid obtained which exhibited all the properties of paratoluic acid. It crystallized from water, and fused at  $178^\circ$ .

It can not be doubted, then, that the bromine product formed by treating ethyltoluene with bromine yields bromparatoluic acid when subjected to the action of chromic acid. The mother-liquors from the first crystallizations of the barium salt were carefully examined, and no evidence was obtained of the presence of a second salt. The oxidizing mixtures were also examined, and nothing but a very small quantity of an acid was found which differed at all from bromparatoluic acid. The quantity of the acid was so small that we were unable to examine it thoroughly. It was found to fuse between  $195^\circ$  and  $200^\circ$ . The barium salt and the acid itself did not differ enough from bromparatoluic acid and its barium salt to make it appear at all improbable that the acid was simply impure bromparatoluic acid.

The interpretation of the transformations here described we believe to be a simple matter. We believe that the methyl group is protected from oxidation because it stands in the ortho-relation to the bromine atom, while the ethyl is oxidized because it stands in the meta-

relation to the usual method of formula of brominating to these ideas, can, at present, be only preliminary, for, un-



bromine. Or, adopting of representation, the ethyltoluene is, according to course, this conclusion be only regarded as preliminary until the results of more

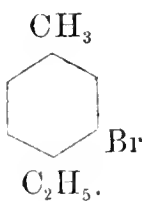
experiments have been described, the hypothesis upon which the proof for this formula is dependent can hardly be considered as established. Assuming the formula to be correct, however, what does it indicate?

We know that when a negative group enters toluene its tendency is to take mainly the para-position. The influence of the hydrocarbon residues is, as is said, to repel the negative group. But, plainly, until we know that the para-position is really further removed than the ortho-position, this statement can only be figurative and directly dependent upon the scheme of Kekulé for its meaning. It is true that the peculiar cases of condensation noticed in connection with ortho-compounds, among which may be mentioned the formation of phthalic anhydride, of salicylic anhydride, etc., etc., do really seem to show that groups in the ortho-position with reference to each other are more closely connected than groups in the other positions; but there are not enough facts known as yet to warrant the expression of a decided opinion upon this subject.

The formation of the bromethyltoluene represented by the formula given shows that one of the groups acts more strongly upon the bromine atom than the other, for, as remarked above, if both groups acted with equal intensity, two isomeric products should have been obtained. While we can not tell which group acts with the greater intensity by examining the formula, the following reasoning seems to be justifiable. If, as is commonly stated,  $\text{CH}_3$  repels negative groups, then we would expect  $\text{C}_2\text{H}_5$  to exert the same kind of action more strongly, as any force exerted by either group must be dependent to some extent upon the mass of the group, and the mass of  $\text{C}_2\text{H}_5$  is greater than that of  $\text{CH}_3$ . Assuming this to be the case, and assuming, further, that the para-position is further removed than the ortho-position, then it would follow that the meta-position is also further removed than the ortho-position, otherwise the bromine ought to take the ortho-posi-

tion with reference to that group which exerts the stronger action.

Although these latter considerations can lead us at present to no positive conclusions, still they are interesting as indicating a possible future method of investigation. The proofs for the structure of bromparatoluic acid are, however, independent of the theory in regard to the nature of benzene.

One objection may be made to the proof. It may be said that even though the conclusion with reference to the protective influence exerted by the bromine upon the group situated in the ortho-position be acknowledged, it would still be possible to obtain bromparatoluic acid from a body of the structure  For the  $\text{CH}_3$  might be converted into carboxyl, and the  $\text{C}_2\text{H}_5$  by the oxidizing mixture, so as to leave  $\text{CH}_3$  in its place. This does not appear probable in the light of all known facts, but still we could easily decide this point by oxidizing bromparadiethylbenzene. If the  $\text{C}_2\text{H}_5$  group can break up in the manner indicated, then the product would be bromparatoluic acid; whereas, if it does not break up, the product will be bromparaethylbenzoic acid.

Among experiments which have been performed by others and which bear upon the question discussed in this paper, may be mentioned those which have proved that, by oxidation of monosubstitution products of cymene (parapropyltoluene), derivatives of paratoluic acid are obtained. Thus Landolph has shown\* that monobromcymene yields monobromparatoluic acid. Fittica† has performed the same experiment with the same result. Fittica‡ has also shown that cymene, when treated with concentrated nitric acid, yields nitroparatoluic acid, which is identical with that obtained by the oxidation of nitroparaxylene, and by treatment of paratoluic acid with nitric acid. It must be stated in this connection, however, that both Landolph and Fittica obtained two mononitro-derivatives from cymene, and, according to Fittica, each of these derivatives yields a different nitro-acid when oxidized. If two nitro-acids can be obtained in this way, it seems possible that one of them may prove to be not nitrotoluic but

\* Ber. d. chem. Gesell., 5, 267.

† Ann. der Chemie, 172, 202.

‡ Loc. cit.

nitroparapropylbenzoic acid. Indeed, according to a recent notice\* by v. Gerichten, the substance formerly described by Landolph and by Fittica as solid nitrocymene has not the composition of nitrocymene at all, hence it may well be doubted whether the product described as a new nitrotoluic acid has the composition ascribed to it. Again Flesch† succeeded in forming sulphotoluic acid by oxidizing thioecymene. Bechler‡ also obtained a sulphotoluic acid in the same way, while Fittica§ states that the sulphotoluic acid which is produced by oxidizing thiothymocymene with nitric acid is not identical with that described by Flesch and by Bechler.

To the cases of the chloreymenes and bromecymenes studied by v. Gerichten reference was made in the preceding article. We may, however, here call attention to the interesting fact that after v. Gerichten's first publication in which he claimed to have prepared two isomeric chlortoluic acids from the two isomeric chloreymenes, we publicly|| expressed doubt in regard to the accuracy of his work, and suggested that one of the chlortoluic acids might prove to be chlorparapropylbenzoic acid. Shortly afterward v. Gerichten published a notice in which he acknowledged that one of his acids had actually the composition of a chlorpropylbenzoic acid as we suggested. Later, however, he believes that he has proved this acid to be ethylchlorhydrocinnamic acid. The uncertainty connected with his last conclusion, however, is so great, as was pointed out in the previous article, that for the present we feel justified in waiting for further proofs of its correctness. We feel this way, particularly as there are now so many cases known which show that the views held by us in regard to the conduct of aromatic substitution products under the influence of oxidizing agents are correct, and there is really only this last one uncertain case which in any way speaks against our views.

\* Ber. d. chem. Gesell., 11, 1091.    † *Ib.*, 6, 481.    ‡ Journ. prak. Chemie, 116, 167.

§ Ann. der Chemie, 172, 323.

|| Ber. d. chem. Gesell., 11, 282.

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NOTE ON THE DETERMINATION OF SILICON  
IN PIG IRON AND STEEL.\*

BY THOMAS M. DROWN.

In experimenting in connection with Mr. P. W. Shimer (now chemist of the Thomas Iron Company, Hokendauqua, Pa.) on methods for the determination of silicon in pig iron, in order to find one which should be accurate and yet give results in a few hours, I have adopted the following procedure, which, as far as my experience goes, leaves nothing to be desired.

About one gram of pig iron or steel is treated in a platinum or porcelain dish with 25 cubic centimeters of nitric acid (sp. gr. 1, 2). When action has ceased, 25 to 30 cubic centimeters of dilute sulphuric acid (one of acid and three of water) are added, and heat applied until the nitric acid is nearly or quite driven off. The heat of a water-bath is sufficient, though the process may be hastened by heating higher on a sand-bath. Water is then cautiously added (as soon as the free sulphuric acid is sufficiently cool) and the contents of the dish heated until the crystals of ferric sulphate are completely dissolved. The solution is then filtered *as hot* as possible, the residue washed first with hot water, then with 25 to 30 cubic centimeters of hydrochloric acid (sp. gr. 1, 12), and finally with hot water. After drying and igniting, the silica will be found to be snow-white and granular.

The following are some results obtained by this method compared, in some instances, with the older method of treatment with nitric acid, evaporation to dryness, heating to 150° C. for several hours, dissolving out the iron in hydrochloric acid, and filtering off from the insoluble residue, which is dried and ignited, and the resulting impure silica fused with alkaline carbonates.

The letters denote different samples of pig iron.

\* Read before the American Institute of Mining Engineers. Communicated by the Author.

	PER CENT. OF SILICON.							
	A	B	C	D	E	F	G	Bessemer steel.
Old method.....	2.64	2.46	.....	1.45	1.65	.....	.....	.672
New method, 1...	2.70	2.47	1.13	1.63	1.53†	1.66	2.50	.676
“ “ 2...	2.68	2.47	1.18	1.62	1.51†	1.68	2.50	.672
“ “ 3...	2.81*	2.47	.....	1.65	1.51†	1.72	2.50	.672
“ “ 4...	.....	.....	.....	.....	1.63‡	1.70	2.47	.....
“ “ 5...	.....	.....	.....	.....	1.65‡	.....	2.46	.....
“ “ 6...	.....	.....	.....	.....	1.65‡	.....	.....	.....

\*Not washed with hydrochloric acid.

†In these analyses hydrochloric acid was used after the addition of nitric acid, and was not completely driven off.

‡Hydrochloric acid was used for solution instead of nitric acid.

Some incidental results obtained in developing this process have enough interest to be worthy of record. Treatment of pig iron with concentrated sulphuric acid, heating till fumes arise, diluting with water, and filtering after all action has ceased, gives a silica which is seldom pure, and yet the results are considerably too low.

Treatment with dilute sulphuric acid and evaporation till the acid fumes in the air, then filtering after dilution, gives occasionally results which are accurate; but this method is uncertain, depending on the fineness of the borings and character and composition of the pig iron. The silica obtained is seldom white. The following are some results obtained in this way :

	PER CENT. OF SILICON.			
	A	B	C	D
Old method .....	1.02	1.64	2.64	3.85
New method, 1.....	1.05	1.73	3.00	3.88
“ “ 2.....	1.05	1.69	2.98	3.91
“ “ 3.....	1.05	1.70	2.97	.....
“ “ 4.....	.....	.....	3.01	.....

Treatment in platinum dishes gave very slightly lower results than porcelain dishes.

If after treatment with dilute sulphuric acid the solution is filtered off from the residue without concentration of the acid, it is found that about one-half of the silicon is in the solution and the other half in the residue; when nitric acid is used and the solution filtered off as soon as all action has ceased, it is found that about two-thirds of the silicon is in the solution and one-third in the residue; and with hydrochloric acid, about one-third goes into the solution and two-thirds remains in the residue. It is not probable that there is any precise ratio existing between the amount of silicon dissolved and the amount in the residue in the case of any one of the acids, the ratio being doubtless variable and depending on the concentration of the acid, the time of action, and the temperature; yet the marked difference in the action of the three acids in this respect is interesting.

The washing with hydrochloric acid of the residue obtained by the action of nitric and sulphuric acids on pig iron is in most cases necessary. Thus there was obtained from the pig iron when water only was used for washing, 2.67 per cent. of silicon against 2.52 when washed with hydrochloric acid; and in another sample, 2.10 per cent. against 1.70 per cent.

Although the results obtained with hydrochloric acid for the original solution of the iron show, as far as the experiments go, as good results as those obtained with nitric acid, yet I prefer the nitric acid treatment on account of the silica obtained being compact and granular, while the use of hydrochloric acid, and also of sulphuric acid alone, yields a silica which is light and flaky.

EASTON, PA., *February, 1879*.

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## ON A NEW BASE.

BY EDGAR F. SMITH.

In the *Proceedings of the Am. Phil. Soc.* for May 4, 1877, and *Jahresbericht*, 1877, Heft i. p. 420, may be found a paper containing a description of several new chlorine derivatives of toluene. One of these, to which especial interest attaches itself, is a *carbon chloride* having the following empirical formula  $C_{21}Cl_{26}$ . It was obtained by treating toluene with dry chlorine until the gas was no longer absorbed. The new derivative when pure formed large colorless prisms which fused at  $152^{\circ}$ – $153^{\circ}C$ . It possessed an odor very much like that of camphor. In water and alcohol it was insoluble, while chloroform dissolved it readily.

*Action of Aniline upon  $C_{21}Cl_{26}$ .*

A quantity of the above compound, finely divided, was heated in a sealed tube with an excess of aniline for six or eight hours. The temperature during this time did not exceed  $180^{\circ}C$ . Upon examination after cooling a deep red colored, viscid product was discovered, which was transferred to a shallow dish, water added, and the whole then heated upon a water-bath. In this manner much of the adherent aniline was expelled. By repeatedly distilling the residue remaining after evaporation it was finally obtained pure.

*Properties.*—The new base produced in the above manner contains chlorine and nitrogen. It forms salts with acids. In water, and indeed all solvents, it is exceedingly easily soluble. From the most concentrated aqueous solutions it is obtained only after long standing, when it separates in thin broad scales, which carbonize slightly at  $225^{\circ}C$ , and fuse at  $230^{\circ}C$ . The crystals are almost colorless; they refract light strongly.

Upon gently heating a portion of the base with an aqueous solution of chromic acid, a reddish brown flocculent mass was precipitated. This was filtered and washed. In hot water it dissolved sparingly; more soluble in alcohol, to which it im-

parted an intense red color. On the addition of zinc and dilute hydrochloric acid to the highly colored solution, the latter was slowly decolorized, but upon warming the liquid the color again appeared.

*Hydrochloric Acid Salt.*—Upon evaporating a portion of the above base with hydrochloric acid and repeatedly recrystallizing the residue, the salt was procured in very long, broad, colorless crystals.

In water and alcohol the salt is readily soluble.

*Analysis.*—.1115 grams dried salt dissolved in water and treated with silver nitrate gave .1283 grams AgCl, yielding .0317 grams Cl, corresponding to 28.43 per cent. chlorine.

The investigation of the various derivatives of  $C_{21}Cl_{26}$  advances slowly owing to the fact that this compound is obtained with great difficulty; the cold of winter is necessary for its formation.

LABORATORY OF THE UNIVERSITY OF PENNA., April 17, 1879.

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## LABORATORY NOTES FROM THE UNIVERSITY OF CINCINNATI.\*

### X.—ON SOME NEW SALTS OF ANILINE.

BY MILES BEAMER AND F. W. CLARKE.

The following salts of aniline, which seem to have been hitherto undescribed, we have lately prepared and partially examined.

*Aniline Chlorate.*—This salt is formed by the direct union of aniline and chloric acid. When aniline is added to a dilute aqueous solution of the acid, white crystals almost immediately appear. These, however, if exposed to the air while damp, are rapidly decomposed, and in the course of a few moments become

\* The earlier numbers of this series of notes appeared in the *American Journal of Science and Arts*, for April and October 1877, and September 1878.

black. A better way to prepare this very unstable body is to cautiously add chloric acid to an alcoholic solution of aniline, and then to evaporate under the receiver of an air-pump. By operating thus upon a small quantity of material in a watch-glass, long, white, slender prisms of over an inch in length were obtained.

Aniline chlorate is very readily soluble in alcohol and ether, but less soluble in water. On exposure to air, or upon even gentle heating, its solutions blacken and decompose. The thoroughly dried substance, however, may be preserved for a day or more without change. It detonates sharply when struck; and in common with other chlorates it decomposes explosively when brought in contact with concentrated sulphuric acid. When heated to  $75^{\circ}$ – $76^{\circ}$  it also explodes. This temperature was fixed by repeatedly heating crystals of the salt upon the surface of mercury into which a thermometer dipped. Heat was cautiously applied to the mercury, and the exploding point was thus ascertained with considerable accuracy.

*Aniline Perchlorate.*—The preparation of this compound was similar to that of the chlorate. Dilute perchloric acid was added to an alcoholic solution of aniline, and the mixture was evaporated *in vacuo*. The crystals are tolerably large rhombic plates, not nearly so unstable as those of the chlorate, and when dry are permanent in the air. They detonate feebly when struck or heated, and are decomposed by sulphuric acid. The exact temperature of decomposition could not be ascertained.

*Aniline Iodate.*—When aniline is added to a solution of iodic acid, this body is copiously precipitated in the form of white scales, which may be dried between folds of filter-paper. It is very slightly soluble in cold water, more soluble in hot water, and more so still in boiling alcohol. From the latter solvent it is deposited on cooling in beautiful nacreous scales. All of its solutions slowly decompose upon standing, and even the dry substance becomes discolored by long exposure to the air. When heated slowly to  $110^{\circ}$  it blackens; but no further change takes place, even when the temperature is carried as high as  $150^{\circ}$ . By sudden heating, however, it explodes at  $125^{\circ}$ – $130^{\circ}$ . On percussion it detonates very feebly, yielding a

dense cloud of smoke which is light brown by reflected, and violet by transmitted light. When thrown upon sulphuric acid it instantaneously decomposes in a similar way, yielding the same dense vapors. Specific gravity 1.48 at 13°.

*Aniline Fluohydrate*.—Beautiful pearly scales formed by the union of aniline and fluohydric acid. It is very soluble in boiling alcohol, but separates out from the solution so rapidly upon cooling as to completely choke up the throat of the funnel through which it is filtered.

*Aniline Phthalate*.—Formed by the addition of aniline to an alcoholic solution of phthalic acid. The salt crystallizes very readily in clusters of concentric needles. Melting-point 145°–146°.

*Aniline Monochloracetate*.—Upon adding aniline to a solution of monochloroacetic acid this salt is soon deposited in a flocculent mass of white crystals. These, when dissolved in warm (not hot) water, and recrystallized *in vacuo*, reappear as long, white, slender needles, of melting-point 88°. By boiling the aqueous solution of the compound it is decomposed.

*Aniline Dichloracetate*.—Formed like the monochloracetate. It crystallizes in long white prisms, which melt at 122°.

*Aniline Trichloracetate*.—Prepared by dissolving aniline in an aqueous solution of trichloroacetic acid. From dilute solutions it is deposited in crystalline plates, piled step-wise one upon another. When crystallized more rapidly, that is, from a more concentrated solution, it appears as large, thin, transparent rhombic plates, somewhat resembling mica. Either form of crystals heated to 50° becomes white and opaque, but undergoes no loss of weight. This opaque modification, recrystallized, is reconverted into the original transparent variety. Melting-point 145°.

Of these salts, the iodate and trichloracetate are being farther investigated.

## XI.—NOTE ON LITHIUM PICRATE.

BY MILES BEAMER AND F. W. CLARKE.

Lithium carbonate dissolves readily in an alcoholic solution of picric acid; and, on spontaneous evaporation, long, slender prisms of anhydrous lithium picrate are obtained. Like other

pierates the salt is bright yellow, and detonates feebly upon percussion. When heated to  $200^{\circ}$  it blackens, but no further change ensues even when the temperature is carried to  $260^{\circ}$ . Heated suddenly in a flame, however, it explodes with great violence. Specific gravity 1.716 at  $19^{\circ}$ ; 1.724 to 1.740 at  $20^{\circ}$ .

## XII.—PRELIMINARY NOTICE OF A NEW VOLATILE ALKALOID.

BY W. L. DUDLEY.

*Spigelia marilandica*, or pink-root, has been known for many years to possess peculiar medicinal properties, seemingly indicative of the presence of an alkaloid. According to the published analysis of the root by M. Fennelle, however, it contains "a fixed and volatile oil, a small quantity of resin, a bitter substance, a mucilaginous, saccharine matter, albumen, gallic acid, the malates of potash and lime, &c., and woody fibre."

Since the activity of *spigelia* is somewhat diminished by time, I suspected the presence of a volatile alkaloid, and began a search for the same. About two kilograms of the dried root were ground, inserted in a flask, mixed thoroughly with milk of lime, and distilled over a paraffin bath. The distillate was collected in a receiver containing hydrochloric acid, and evaporated to dryness over a water-bath. The residue was then extracted with absolute alcohol, the solution filtered and allowed to evaporate spontaneously to dryness. A small amount of crystalline substance remained, which was soluble in water, and which gave the following reactions, differing from those of the previously known volatile alkaloids. In the accompanying table these reactions are compared with some of those given by nicotina, conia, and lobelina:—

	<i>Spigelia.</i>	<i>Nicotina.</i>	<i>Conia.</i>	<i>Lobelina.</i>
Iodine in a KI solution.	Brownish red precipitate.	Brownish red precipitate.	Pale brownish red precipitate.	Brownish red precipitate.
Potassio-mercuric iodide.	White crystalline precipit.	Yellowish precipitate.	Like nicotina.	Pale yellow precipitate.
Metatungstic acid	White flocculent precipit.			

The precipitate formed by potassio-mercureic iodide with spigelina is soluble in acids, in alcohol, and in ether, but insoluble in an excess of the precipitant. In these points it differs clearly from the precipitates given by the other volatile alkaloids.

An insufficient supply of material rendered farther investigation at the time impossible; but enough was done to distinctly indicate the presence of a new volatile base, to which I naturally apply the name of spigelina.

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## ON HEPTANE FROM PINUS SABINIANA.\*

BY T. E. THORPE, PH. D., F. R. S.,

*Professor of Chemistry in the Yorkshire College, Leeds.*

In a paper read to the California Pharmaceutical Society on December 13, 1871, and reprinted in the *Pharmaceutical Journal* for March 30, 1872, Mr. William Wenzell, of San Francisco, describes as new and under the name of *Abietenet*† a hydrocarbon obtained by distilling the terebinthinate exudation of a coniferous tree, *Pinus sabiniana*, Dougl. This tree is indigenous to California, and grows on the dry slopes of the foothills of the Sierra Nevada, and on the hills along the coast; it appears to be pretty plentiful, and is known locally as the nut pine or Digger pine, names suggested by the circumstance that the Digger Indians rely to some extent on its fruit for food.

In order to procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil is met with in San Francisco as an article of

\* Communicated by the Author.

† The name *Abietin* was applied by Callot to a resin obtained from the turpentine of *Abies picea* and *Abies balsamea*.

commerce, and during the last few years has acquired some reputation under the names of "abietene," "erasine," "aurantine," "theoline," &c., as a substitute for "benzoline" or "petroleum benzene" for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colorless mobile liquid of powerful aromatic smell, recalling that of oil of oranges. The crude oil, according to Mr. Wenzell, boils almost entirely between  $100^{\circ}$  and  $105^{\circ}$ , and on redistillation the liquid is obtained of the constant boiling-point of  $101^{\circ}$ . The portion boiling above  $105^{\circ}$  leaves on evaporation a small quantity of a resinoid body, possessing the strong penetrating odor of the original product. The liquid is highly inflammable and burns with a brilliant white smokeless flame. Its vapor is powerfully anæsthetic, and it has been used with success as an insecticide.

No analysis or vapor-density determination of this liquid is given in the communication above referred to, nor does Mr. Wenzell offer any opinion as to its real nature. He contrasts its characters with those of terebene (spirits of turpentine), the hydrocarbon obtained from *Pinus palustris*, *P. sylvestris*, &c., and points out the very striking differences observed in their physical and chemical properties. Abietene has a sp. gr. of 0.694 at  $16.5^{\circ}$ , whilst that of terebene is 0.840 at about the same temperature. Oil of turpentine boils at  $160^{\circ}$ , whilst the boiling-point of abietene is  $101^{\circ}$ . Hydrochloric acid gas is but slightly dissolved by abietene, whereas oil of turpentine absorbs it with avidity. Nitric acid acts violently on oil of turpentine; it has little or no action on abietene in the cold.

Abietene was evidently sufficiently remarkable to merit further investigation. From its general behavior towards reagents it seemed not unlikely that it would prove to be a paraffin, and the boiling point and sp. gr. appeared to indicate *normal heptane*. The occurrence of heptane, or indeed of any other paraffin, playing the part of oil of turpentine in the vegetable kingdom was hitherto unheard of. The only natural source of this hydrocarbon was petroleum or some of the fossil-fish oils obtained in Greenland, Switzerland, and other places. Menhaden oil contains considerable quantities of heptane, and it is met with among the products of the destructive distillation of cannel and shale.

Through the kindness of Mr. H. B. Brady, F. R. S., I was able to obtain, through Dr. Squibb, of New York, about a couple of gallons of abietene from Mr. Wenzell. The crude oil fully answered the description already given of it by the latter gentleman. It was almost colorless, and had the strong persistent odor of oil of oranges. It began to boil slightly below  $100^{\circ}$ , and the greater part distilled below  $101^{\circ}$ . The residual portion darkened slightly, and on evaporation left a small quantity of resinoid matter of a brown color which had the peculiar smell of the liquid in a very high degree. This led to the supposition that the odor of the crude oil might be due in great part to the resin in solution, and further examination proved this to be the case. On agitating it for some time with oil of vitriol, the acid became brown, and on again distilling the hydrocarbon was found to have lost its smell of orange oil.

Two determinations of its boiling-point were made by the aid of a thermometer capable of being read to  $0.01^{\circ}\text{C}$ . The first observation gave  $98.27^{\circ}$  at 755.6 mm., the second  $97.93^{\circ}$  at 746.9 mm. The mercurial columns in both cases were wholly immersed in the vapor, and the barometric pressures are corrected and reduced to  $0^{\circ}\text{C}$ . Assuming the validity of the well-known expression—

$$T = t + 0.0375(b - 760),$$

where  $t$  is the observed boiling point and  $b$  the barometric pressure, the boiling point,  $T$ , under the standard pressure becomes respectively—

I.	.	.	.	98.43°
II.	.	.	.	98.42

The first determination was made on about three litres of the liquid, the second on about 250 cc., after a second treatment with a mixture of nitric and sulphuric acids; in both cases the liquid boiled as constantly as distilled water. In all I obtained about seven litres of the perfectly pure substance from seven and a half litres of the crude oil.

That abietene is actually heptane is proved by the following analyses and determinations of vapor-density :

I. 0.3500 gram hydrocarbon gave 1.0754 gram  $\text{CO}_2$  and 0.5050 gram  $\text{O}_2\text{H}$ .

II. 0.3000 gram hydrocarbon gave 0.9215 gram  $\text{CO}_2$  and 0.4336  $\text{H}_2\text{O}$ .

Calculated for $\text{C}_7\text{H}_{16}$ .			Found.	
			I.	II.
C	...	83.97	83.85	83.78
H	...	16.03	16.03	16.06
		<hr/>	<hr/>	<hr/>
		100.00	99.88	99.84

Two determinations of its vapor-density, made in a modified form of Hofmann's apparatus,\* gave the following results:

I. Weight of liquid ..... 144.5 mgm.  
 Volume of vapor (corrected for expansion of glass, error of meniscus, &c).. 90.39 cc.  
 Temperature of vapor..... 99.90°C.  
 Barometer (corrected and reduced)... 757.6 mm.  
 Height of mercury in tube (reduced) 387.8 "

II. Weight of liquid ..... 76.9 mgm.  
 Volume of vapor (corrected) ..... 69.77 cc.  
 Temperature..... 99.60° C.  
 Barometer ..... 749.0 mm.  
 Height of mercury in tube ..... 493.4 "

Calculated for $\text{C}_7\text{H}_{16}$ .	Found.	
	I.	II.
49.90	50.07	49.94

### I. *The Physical Characters of Heptane from Pinus Sabiniana.*

The possession of so large a quantity of perfectly pure heptane has induced me to study some of the physical characters of this hydrocarbon. These observations have included the determination of its specific gravity, and the measurement of its thermal expansion, refractive index, optical activity, viscosity, and superficial tension.

*Specific Gravity.*—Three determinations of specific gravity made with different bottles gave the following results:

\* The apparatus here referred to allows of the determination of a vapor-density with almost as much exactitude as that of any other physical constant; it was designed more especially with a view of controlling the purity of some liquids employed in a research involving the determination of a number of thermal expansions.

0.68848 at 14.98°

0.68855 " 14.87

0.68858 " 14.87

compared with water at the same temperatures respectively. The weighings were made by the method of vibrations and the weights are reduced to a vacuum. Reducing these results by the aid of Rossetti's tables for the expansion of water, and by means of the formula for the thermal expansion of heptane given below, the specific gravity at 0°, compared with water at 0°, becomes respectively—

0.70057

0.70055

0.70058

---

 Mean... 0.70057

*Thermal Expansion.*—The rate of expansion of the heptane was determined by heating the hydrocarbon in dilatometers properly calibrated and graduated. The volume of the hydrocarbon at 0° was obtained by immersing the dilatometers in melting snow. The instruments were then placed in a large copper bath fitted with plate-glass sides, and holding several litres of water, which could be kept in constant motion by stirrers worked by a small hydraulic engine. The water was heated by steam and the temperature ascertained by thermometers capable of being read to 0.01° C.

Two series of observations were made. The first set gave the following results :

Tempera- ture.*	Observed volume.	Calculated volume.	Tempera- ture.	Observed volume.	Calculated volume.
0.00	3290.1	3290.4	53.71	3516.3	3516.9
9.04	3326.1	3326.0	62.80	3560.1	3559.9
17.27	3359.2	3359.1	72.12 "	3606.2	3605.7
26.96	3398.9	3399.1	80.68	3649.5	3649.5
35.55	3435.9	3435.7	87.32	3684.2	3684.6
44.96	3477.2	3477.1	93.70	3719.9	3719.4

\*These temperatures are expressed in degrees of the air thermometer in order to make them uniform with my other observations of thermal expansion. The conversion from the ordinary thermometric values is effected by a table compiled from Regnault's and Recknagel's comparisons of the air and mercurial thermometers (see Wuellner's *Lehrbuch der Physik*). To convert the degrees of the air thermometer into those of the mercurial thermometer *add* 0.08° at 10°, 0.16° at 25°, 0.16° at 65°, 0.1° at 80°.

Combining the results by the method of equation of conditions, we obtain the formula —

$$3290.361 + 3.895352 t + 0.00432087 t^2 + 0.00003183 t^3,$$

by means of which the numbers in the third column of the above table are calculated.

The second series, made in a different dilatometer, gave the following data:

Tempera- ture.	Observed volume.	Calculated volume.	Tempera- ture.	Observed volume.	Calculated volume.
0 00	2879.6	2879.3	53.71	3076.4	3077.0
9 04	2910.5	2910.6	62.81	3114.5	3114.5
17.27	2939.3	2939.5	72.13	3155.2	3154.7
26.97	2974.2	2974.5	80.68	3193.6	3193.2
35.54	2006.4	3006.2	87.27	3223.8	3224.1
44.96	2042.3	3042.3	93.71	3255.3	3255.4

These numbers afford the expression —

$$2879.302 + 3.432882 t + 0.00247831 t^2 + 0.00003964 t^3,$$

by the aid of which the numbers in the third column of the above table are computed.

Dividing through by the first terms respectively, and correcting for the expansion of the glass of the dilatometers (0.00002130 for 1° in Series I, and 0.00002303 in Series II), the formulæ become—

I.  $1 + 0.00120517 t + 0.00000133841 t^2 + 0.000000009701 t^3$ ,  
and

II.  $1 + 0.00121529 t + 0.00000088819 t^2 + 0.000000013787 t^3$ .

The mean formula is —

$$1 + 0.00121023 t + 0.0000011133 t^2 + 0.00000001174 t^3,$$

by the aid of which the following table, showing the relative volumes of heptane from *Pinus sabiniana* at every 5° between 0° and 100° is calculated —

Tempera- ture.	Volume.	Difference.	Tempera- ture.	Volume.	Difference.
0	100000	—	55	107188	712
5	100608	608	60	107916	728
10	101222	614	65	108659	743
15	101844	622	70	109420	761
20	102474	630	75	110198	778
25	103114	640	80	110995	797
30	103763	649	85	111812	817
35	104423	660	90	112650	838
40	105094	671	95	113509	859
45	105778	684	100	114390	881
50	106476	698			

The volume at the boiling point 98.43 is 1.14111; hence the specific gravity at this temperature is 0.61393, which gives for heptane the *specific volume* 162.54. Kopp's values (C = 11; H = 5.5) afford the number 165.

*Refractive Index*.—A careful set of observations of the index of refraction of heptane from *Pinus sabiniana* was made for me by Mr. John I. Watts in the Physical Laboratory of the Owens College, Manchester, by one of Elliott's horizontal goniometers.

Five concordant determinations of the angle of the prism employed gave as a mean result:

$$\theta = 59^{\circ} 12' 20''.$$

The same number of observations of the angle of minimum deviation gave:

$$\delta = 27^{\circ} 21' 44''.$$

The source of light was a sodium flame. The temperature of the liquid was 17.6°.

Inserting these numbers in the the well-known formula

$$\mu = \frac{\sin. \frac{1}{2} (\delta + \theta)}{\sin. \frac{1}{2} \theta},$$

we obtain 1.3879 as the refractive index for D.

The *specific refractive energy*,  $\frac{\mu - 1}{d}$ , where  $d$  is the specific gravity of the liquid at 17.6° is 0.565; whence the *molecular*

*refractive energy* is 56.4 in close accordance with the computed number 55.8, calculated by Landolt's values,  $C = 5$ ,  $H = 1.3$ .

*Optical Activity.*—It is well known that the various terpenes are optically active, often to a very remarkable extent; hence a special interest seemed to be attached to the question of the behavior of the heptane of *P. sabiniana* towards polarized light. Through the kindness of Prof. Gamgee, Mr. J. H. Poynting was able to make a number of observations on the hydrocarbon by means of an excellent Laurent's polarimeter belonging to the Physiological Laboratory of the Owens College. These observations seem to indicate that the heptane does actually rotate the plane of the polarized ray, although to a very slight extent only, a column 200 mm. long exhibiting a rotatory power of  $+6.9'$ . This amount is so small that I was disposed to attribute it to the possible presence of impurities, despite the careful rectification to which the hydrocarbon had been subjected: the original exudation might have contained small quantities of a terpene, or a minute trace of the resinous matter which it has been stated the crude oil leaves on evaporation might still be contained in the distilled hydrocarbon. The liquid with which Mr. Poynting experimented was accordingly agitated with a mixture of concentrated nitric and sulphuric acids at frequent intervals for several days, but the acids remained perfectly colorless, and the hydrocarbon after redistillation showed precisely the same rotatory power as before, viz.,  $+6.9'$ . I am inclined to believe, however, that an optically active terpene is actually present in crude abietene, although not to a greater extent than 0.5 per cent.: the liquid residue left on distilling the crude oil boiled between  $140^\circ$  and  $160^\circ$ , and showed a rotatory power of  $-12^\circ 23.5'$ : this liquid, it should be noted, had not been treated with acids. The resin itself, in alcoholic solution, appears to be optically inactive.

*Viscosity.*—The capillary transpiration of the heptane from *Pinus sabiniana* was determined by a method identical in principle with that already employed by Poiseuille, Graham, and others; this consists in noting the time required for a given volume of the liquid at some particular temperature and under a uniform pressure to flow through a cylindrical capillary tube of known dimensions. The capillary tube employed was

85.4 mm. in length and 0.2105 mm. in internal diameter; it was sealed, at right angles, to a long cylindrical bulb, containing between two marks etched on the narrow tube above and below the bulb 14.7755 cc. The open end of the capillary tube was connected with a receiver, and the whole was so arranged that it could be wholly immersed in a large bath fitted with plate-glass sides and holding several gallons of water. The temperature of the bath, and therefore of the hydrocarbon contained in the bulb and tubes, could be raised to any desired point below about  $80^{\circ}$  by heating a coil of copper tube affixed to the side of the bath through which the water from the bath continually circulated. The liquid in the bath was kept in constant agitation by means of stirrers worked by a small hydraulic engine; and the temperature was ascertained by a thermometer capable of being read to  $0.01^{\circ}\text{C}$ . The hydrocarbon was drawn into the bulb by the aid of the air-pump, and as soon as it had acquired the temperature of the bath it was forced through the capillary tube by the pressure of a confined volume of air kept at a nearly constant tension of 111.2 mm. of mercury by the weight of a column of water of uniform height; and the times at which the level of the liquid passed the two marks, as observed through a telescope, were noted on a chronometer. This apparatus has been employed by Mr. John Muir, student in the Laboratory of the Yorkshire College, in the determination of the viscosity coefficients of a number of liquids; a detailed description of it is reserved for a communication containing the results of his experiments.

Two independent series of observations were made with heptane with the following results:—

*Series I.*

Temperature.	Time (seconds).	V.	$\eta$ .	Temperature.	Time (seconds).	V.	$\eta$ .
6.72°	931.7	7313	.005268	35.07°	611.1	11151	.003454
10.27	794.3	8579	.004490	40.16	582.2	11704	.003292
15.31	749.3	9094	.004236	44.75	560.4	12159	.003168
20.05	710.9	9585	.004019	49.70	534.7	12745	.003023
25.06	673.8	10113	.003810	54.84	512.0	13309	.002895
29.95	642.9	10599	.003635				

## Series II.

Temper- ature.	Time (seconds).	V.	$\eta$ .	Temper- ature.	Time (seconds).	V.	$\eta$ .
7.09°	845.0	8064	.004777	30.06°	639.6	10654	.003616
10.31	792.9	8594	.004482	35.03	611.6	11141	.003457
15.30	749.3	9094	.004236	39.16	585.2	11645	.003300
20.15	713.0	9557	.004031	45.37	555.7	12262	.003142
25.09	673.6	10116	.003808	49.30	538.0	12666	.003042

The transpiration times are corrected for any slight irregularities in the pressure (these never exceeded 0.4 mm. of mercury), and for the change in the dimensions of the bulb and capillary tube by heat.

If  $Q$  be the volume of the liquid flowing through the tube in the time  $t$ ,  $p$  the pressure under which it is driven expressed in millimeters of water,  $l$  the length of the tube, and  $r$  its radius in millimeters, then the volume,  $V$ , in cubic millimeters flowing in one second of time through a tube 1 mm. long, 1 mm. radius, and under a pressure of 1 mm. of water, on the assumption that Poiseuille's laws hold good under these conditions is given by the formula—

$$V = \frac{Q \cdot l}{t \cdot p \cdot r^4}$$

The numbers so obtained are given in the third column of the above tables.

If all the particles of the moving liquid are flowing in parallel straight lines, with velocities proportional to their distances from a plane parallel to these lines, then of any two contiguous layers, the motion of that which moves the more rapidly will be retarded by a force (viscosity) dependent, *cæteris paribus*, on the nature of the liquid, and varying with its temperature. The coefficient of viscosity in absolute measure is the force expressed in dynes thus exerted on a liquid surface one square centimeter in area, lying in a plane of uniform velocity, when the difference of the velocities of two layers one centimeter apart is one centimeter per second.

The viscosity coefficients,  $\eta$ , of heptane for the particular

temperature given in the table are directly obtained from the values of  $V$  in absolute measure by the expression—

$$\eta = \frac{\pi \cdot 98.1}{8 \cdot V}$$

by means of which the numbers in the last columns of the above tables are calculated.

It will be noticed that the viscosity suddenly diminishes at some point between  $8^\circ$  and  $10^\circ$ . After the latter temperature has been reached the rate of diminution is very regular, and may be represented by an expression of the form—

$$\eta = a + bt + ct^2.$$

Combining all the observations in both series of experiments made at temperatures above  $15^\circ$  by the method of equation of conditions, we obtain the formula—

$$\eta = 0.005003 - 0.00005561 t + 0.0000003061 t^2,$$

which gives results in close accordance with the observed mean values, as the following comparison between the experimental and computed values shows:—

$t^\circ$ .	$\eta$ .		Differ- ence.	$t^\circ$ .	$\eta$ .		Differ- ence.
	Observed	Calcu- lated.			Observed	Calcu- lated.	
15.31	.004236	.004233	.000003	39.66	.003300	.003303	.000003
30.10	.004025	.004021	.000004	45.06	.003155	.003145	.000010
25.07	.003809	.003816	.000007	49.50	.003032	.003031	.000001
30.01	.003625	.003623	.000003	54.84	.002895	.002907	.000012
35.05	.003456	.003451	.000005	98.43	—	.002554	—

*Surface Tension.*—The superficial tension of the heptane from *P. sabiniana* was determined (1) by observations on the rise of the hydrocarbon in a cylindrical capillary tube of known diameter, and (2) by measurements of the form of an air-bubble placed under a plate of glass held under and parallel to the surface of the liquid.

In the first series of observations the apparatus was so arranged that the relation of the surface tension to the temper-

ature could be ascertained from observations on the rise of the liquid in the same tube at different temperatures. A detailed description of the apparatus is reserved for a communication giving the results of an extended series of observations on the surface tension of liquids with special reference to their chemical relations. The measurements were made by the aid of a cathetometer reading to 0.02 mm., and each result is the mean of some six or eight observations. Diameter of tube 0.2531 mm.

Temperature. °C.	Height from the outside level of the liquid to the lowest point of the meniscus in the capillary tube. Observed.	Calculated.	Difference.
7.0	49.62 mm.	49.76	+ 0.14
15.6	48.36	48.20	— 0.16
23.8	46.70	46.71	+ 0.01
30.2	45.58	45.54	— 0.04
38.4	43.99	44.05	+ 0.06
45.5	42.72	42.76	+ 0.04
54.6	41.12	41.11	— 0.01
60.4	40.10	40.05	— 0.05
69.5	38.44	38.39	— 0.05
76.8	36.99	47.07	+ 0.08

No correction has been made for the increase in the diameter of the tube with the temperature. The correction for a difference of temperature of 100° would not affect the fourth place of decimals in the value of the diameter. Combining the observations by the method of least squares, we find that the height of the liquid in the capillary tube may be accurately represented by the expression —

$$h = 58.032 - 0.1818 t.$$

The values calculated by this formula are given in the third column of the above table.

The above formula for a tube 1 mm. in radius becomes —

$$H = 6.4581 + 0.0230067 t.$$

If the constant of capillarity ( $a$ ) be considered as half the weight in milligrams of a column of liquid, of which the area

of the base is 1 square millimeter, and of which the height is that of a column of liquid in a tube 1 mm. radius, then —

$$a = \frac{H \cdot s}{2}$$

in which  $s$  is the specific gravity of the liquid. This for heptane at  $0^\circ$  is —

$$a = \frac{6.4581 \times 0.70057}{2} = 2.2621 \text{ mgm.}$$

Neglecting the angle of capillarity, which, as the observations with the air-bubble show is certainly not very far from  $180^\circ$ , the surface tension in C. G. S. units at  $0^\circ$  is—

$$T = 2.2621 \times 9.81 = 22.19,$$

and its relation to the temperature is expressed by —

$$T = 22.19(1 - 0.003563 t).$$

The observations with the air-bubble were made practically in the manner described by Quincke.\* A rectangular trough  $2\frac{1}{2}$  inches broad, 3 inches long, and 1 inch deep, made of plane parallel plates of glass, cemented together at the edges, was levelled before the cathetometer and filled with the heptane, and another plate of glass was then immersed in the liquid to a depth of a few millimeters, and carefully adjusted until it was parallel with the surface. A bubble of air about 30 mm. in diameter was then blown under the glass by means of a bent capillary tube, and its depth ( $K$ ), together with that of the point where its tangent plane was vertical ( $k$ ), was determined by the cathetometer.

The value of the superficial tension in C. G. S. units is given by the expression —

$$T = \frac{1}{2}(K - k)^2 g s.$$

In the first set of observations ten readings of  $K$  and  $k$  were taken. The temperature was  $15^\circ$ .

$$K = 3.622 \text{ mm.}$$

$$k = 1.083$$

$$g = 9.81 \quad "$$

$$s \text{ at } 15^\circ = 0.6882.$$

$$\text{Hence } T = 21.80.$$

\* Pogg. Ann. 139, 1.

In the second set five readings of  $K$  and  $k$  were taken on another bubble. The temperature was  $10^{\circ}$ .

$$K = 3.452 \text{ mm.} \quad k = 0.960. \quad s = 0.6922.$$

$$\text{Hence } T = 21.12.$$

These numbers agree very well with those deduced from the height of the liquid in the capillary tube.

The method of measurement was scarcely accurate enough to afford any very reliable value of the angle of capillarity. This is given by the formula —

$$\text{Cos. } \theta = \frac{K^2}{(K - k)^2} - 1.$$

Combining all the observations, we find the angle of capillarity of heptane  $167^{\circ}$ . It is worthy of note that the heptane from *Pinus sabiniana* has the lowest surface tension of any liquid yet measured.

Since the superficial tension of a liquid entirely vanishes at the critical point, that is, at the temperature at which the gaseous and liquid states become continuous, the expression  $1 - .003563t$  may afford us an approximation to the critical point of heptane, if we assume that the rate of diminution in capillarity is represented by this formula at high temperatures. We thus find the critical point of the heptane to be  $281^{\circ}$ .

Whether the heptane from *Pinus sabiniana* is absolutely identical with that boiling at about the same temperature obtained from petroleum and shale oil remains to be established. The existing evidence, so far as it goes, seems to indicate that the hydrocarbons are really isomeric.

In May 1874, Professor Schorlemmer, to whom I am indebted for a number of organic preparations for determination of certain of their physical constants, kindly sent me a quantity of normal heptane from petroleum, which he believed to be practically free from the isomeride boiling at  $90^{\circ}$ , and from octane. I found it to boil constantly between  $98.1^{\circ}$  and  $99.1^{\circ}$  under a pressure of 765 mm. Its specific gravity at  $0^{\circ}$  compared with water at  $4^{\circ}$  was 0.7299.

In May 1877, Professor Schorlemmer sent me a second sample of petroleum heptane which had been prepared with special care. This I found to boil between  $98.1^{\circ}$  and  $98.6^{\circ}$  under a barometric pressure of 750.3 mm.

A determination of its vapor-density afforded the following data:—

Weight of hydrocarbon.....	150.7 mgm.
Volume of vapor.....	91.28 cc.
Temperature.....	$99.8^{\circ}$ C.
Pressure.....	381.3 mm.

Calculated.  
49.9

Observed.  
50.1

Two determinations of its specific gravity at  $0^{\circ}$  compared with water at  $4^{\circ}$  gave —

I.....	0.7301
II.....	0.7301

numbers which are almost identical with that afforded by the first sample, and much higher than that of the heptane from *P. sabiniana*, viz., 0.70057.

On the other hand, the hydrocarbon from *P. sabiniana* has precisely the same specific gravity as that of the heptane obtained by heating azelaic acid with caustic baryta. Dale found that the latter body boils at  $98^{\circ}$ – $99^{\circ}$ , and has a specific gravity of 0.6851 at  $17.5^{\circ}$ ; Schorlemmer, who procured the same hydrocarbon in larger quantity, observed 0.6840 at  $20.5^{\circ}$ . Reducing these observations by means of the formula given on page 160, they become respectively —

I.....	0.6992
II.....	0.7000.

If, as Schorlemmer believes, the heptanes from azelaic acid and petroleum are probably identical, the difference in their specific gravities is at present inexplicable. We are now engaged on a joint investigation on the chemical constitution of the heptane from *P. sabiniana*, which may incidentally throw light on this question.

## ON THE LIQUID TOLUENESULPHOCHLORIDE.

BY C. FAHLBERG,

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It is stated in an article by H. Beckurts\* that a third toluenemonosulphonic acid exists in the crude mixture resulting from the action of sulphuric acid upon toluene. Although Beckurts's acid showed differences when compared with the well known tolueneparasulphonic acid and the tolueneorthosulphonic acid, he neglected to prepare oxybenzoic acid from it and to prove its constitution. At the same time he gives his acid the name toluenemetasulphonic acid, and asserts that it is identical with the acid prepared by Mueller† from orthobromtoluenesulphonic acid, by Pagel‡ from orthotoluidinesulphonic acid, and by v. Pechmann§ from paraamidotluenemetasulphonic acid.

It was necessary to repeat his experiments for the purpose of preparing large quantities of tolueneorthosulphamide from the liquid toluenesulphochloride. In doing this my attention was directed to his article, from which I hoped to receive some benefit. On examining his method, however, I preferred for the final separation of the amides to use water instead of alcohol, to which Beckurts refers as a good solvent. My object in doing this was to avoid the changes which alcohol undergoes when an alcoholic solution is treated with bone-black as in the usual process of decoloration. With the exception of this modification I introduced no changes, but adhered strictly to Beckurts's own statements. As Beckurts's amide, fusing at  $104^{\circ}$ – $105^{\circ}$ , is more easily soluble in water than the tolueneorthosulphamide from which the separation of the former had to be effected, I could expect a separation similar to that obtained by Beckurts.

If the liquid toluenesulphochloride || is treated with an

\* Ber. d. chem. Gesell., 10, 943.

† Ann. der Chemie, 169, 47.

‡ Ann. der Chemie, 176, 291.

§ Ann. der Chemie, 173, 202.

|| The liquid toluenesulphochloride was cooled several times in a cooling mixture to  $-15^{\circ}$ , until no more of the solid tolueneparasulphochloride could be separated.

aqueous solution of ammonia and the products are allowed to cool off, there results:

I. A solution above the separated amides, consisting of an excess of ammonia, ammonium chloride, and an unknown organic substance. On evaporating this solution an oil of a dark brownish appearance separated out. Boiled with bone-black several times, fine long needles with a lustre were obtained. These needles had, after recrystallization, a constant fusing point of  $186^{\circ}$ – $187^{\circ}$ . They were found to be identical with Blomstrand's  $\alpha$ -toluenedisulphamide.

II. A solid, yellowish-looking, mixed amide. This amide was subjected to a fractional solution whereby only one portion dissolved, while the other portion remained undissolved. The undissolved portion, *a*, and the dissolved portion, *b*, were treated separately.

*a*. This was dissolved in water, and decolorized two or three times with bone-black, when an amide separated out, fusing at  $153^{\circ}$ – $154^{\circ}$ . This amide gave pure salicylic acid, fusing at  $156^{\circ}$ , when fused with caustic potash; it was pure tolueneorthosulphamide.

*b*. From the hot filtered solution an amide separated, fusing at  $125^{\circ}$ . This was subjected to the same operation as given under II. The undissolved portion, *a*, and the dissolved portion,  *$\beta$* , were again treated separately.

*a*. This was dissolved in water and decolorized several times, when an amide separated out, fusing at  $150^{\circ}$ – $152^{\circ}$ . Recrystallized from pure water, the fusing point became  $153^{\circ}$ – $154^{\circ}$ . This was a second portion of tolueneorthosulphamide.

*$\beta$* . From the hot filtered solution an amide crystallized, fusing at  $120^{\circ}$ . It was recrystallized with bone-black. The fusing point fell to  $115^{\circ}$ . Twice more subjected to bone-black and crystallization, the fusing points became 1st.  $110^{\circ}$ , and 2d.  $108^{\circ}$ . Recrystallized from pure water the fusing point did not change. This was the supposed Beckurts's toluenemeta-sulphamide.

For the reason that tolueneorthosulphamide is very difficultly soluble in cold water, I evaporated in one portion the mother-liquors under II., and obtained from them more of Beckurts's amide, fusing this time at  $105^{\circ}$ . Some undecolorized amide in the mother-liquor caused this change in the fusing point from  $108^{\circ}$  to  $105^{\circ}$ .

In this way I succeeded in separating three amides which differed distinctly in their fusing points.

From 150 grams of liquid toluenesulphochloride I obtained: 15 grams toluenedisulphamide fusing at  $186^{\circ}$ – $187^{\circ}$ ; 15 grams Beckurts's amide fusing at  $105^{\circ}$ – $108^{\circ}$ ; and 100 grams toluene-orthosulphamide fusing at  $153^{\circ}$ – $154^{\circ}$ . I obtained on analysis of the amide fusing at  $186^{\circ}$ – $187^{\circ}$  the following results:

I. 0.2353 grams of the amide gave 0.4370 grams  $\text{BaSO}_4 = 0.060017$  grams S = 25.50 per cent. S.

II. 0.371 grams substance gave 36 cc. N at 758 mm. pressure and  $21^{\circ}\text{C} = 11.00$  per cent. N.

Its analysis showed it to have the composition  $\text{C}_7\text{H}_{10}\text{S}_2\text{N}_2\text{O}_4$ .

	Calculated.		Found.
$\text{C}_7\text{H}_{10}\text{O}_4$	158	63.20	...
S <sub>2</sub>	64	25.60	25.50
N <sub>2</sub>	28	11.20	11.00
	<hr/>	<hr/>	
	250	100.00	

I obtained on analysis of the amide fusing at  $105^{\circ}$ – $108^{\circ}$  the following results:

I. 0.2005 grams of the amide gave 0.27545 grams  $\text{BaSO}_4 = 0.03783$  grams S = 18.85 per cent. S.

II. 0.3674 grams substance gave 26.80 cc. N at 759.5 mm. pressure and  $19^{\circ}\text{C} = 8.40$  per cent. N.

Its analysis showed it to have the composition  $\text{C}_7\text{H}_9\text{SNO}_2$ .

	Calculated.		Found.
$\text{C}_7\text{H}_9\text{O}_2$	125	73.11	...
S	32	18.71	18.85
N	14	8.18	8.40
	<hr/>	<hr/>	
	171	100.00	

I obtained on analysis of the amide fusing at  $153^{\circ}$ – $154^{\circ}$  the following results:

I. 0.2015 grams of the amide gave 0.2747 grams  $\text{BaSO}_4 = 0.037725$  grams S = 18.72 per cent. S.

II. 0.39765 grams substance gave 28 cc. N at 763 mm. pressure and  $16^{\circ}\text{C} = 8.21$  per cent. N.

Its analysis showed it to have the composition  $\text{C}_7\text{H}_9\text{SNO}_2$ .

	Calculated.		Found.
$C_7H_9O_2$	125	73.11	...
S	32	18.71	18.72
N	14	8.18	8.21
	<hr/> 171	<hr/> 100.00	

It is evident from these analyses that the amide fusing at  $186^{\circ}$ – $187^{\circ}$  is a toluenedisulphamide, while the amides one of which fuses at  $105^{\circ}$ – $108^{\circ}$  and the other at  $153^{\circ}$ – $154^{\circ}$  are toluenemonosulphamides, the latter being the well-known tolueneorthosulphamide.

After having concluded the oxidation of the tolueneorthosulphamide upon which a short article by Professor REMSEN and myself has been published\*, I proceeded to oxidize the amide fusing at  $105^{\circ}$ – $108^{\circ}$ .

The results reached by the oxidation were found to be contradictory to the statements made by Beckurts. The amide fusing at  $105^{\circ}$ – $108^{\circ}$  became oxidized in the same way as described in the paper on the oxidation of tolueneorthosulphamide, in which the permanganate of potassium was the agent used. The oxidized solution was evaporated to  $\frac{1}{5}$  or  $\frac{1}{6}$  of the original volume. Before the addition of hydrochloric acid, the solution tasted sweet, reminding one of the anhydroorthosulphaminebenzoic acid. With the possibility in view that anhydroorthosulphaminebenzoic acid might be present, I proceeded to a careful investigation of this solution. On adding hydrochloric acid, parasulphaminebenzoic acid was precipitated and proved beyond a doubt to have the same properties as the acid produced from pure tolueneparasulphamide. The paraoxybenzoic acid which was prepared from it fused at  $210^{\circ}$ . The filtered solution from parasulphaminebenzoic acid was evaporated to dryness and the residue treated with alcohol. From the alcoholic solution there was obtained a substance in every respect identical with anhydroorthosulphaminebenzoic acid. The salicylic acid produced from it fused at  $156^{\circ}$ . That part of the residue which was undissolved by the alcohol was found to contain the acid potassium salt of orthosulphobenzoic acid and potassium chloride; the former when fused with caustic potash gave salicylic acid fusing at

\* Ber. d. chem. Gesell., 12, 469.

156°, just as in the case of anhydroorthosulphaminebenzoic acid. Since we know only one oxidation product from tolueneparasulphamide and two oxidation products from tolueneorthosulphamide, Beckurts's amide fusing at 105°–108° corresponded, according to this experiment, to a mixture of tolueneparasulphamide and tolueneorthosulphamide. The products of this oxidation mentioned above are: parasulphaminebenzoic acid, anhydroorthosulphaminebenzoic acid and acid potassium orthosulphobenzoate. There was nothing left to support the belief in the existence of Beckurts's toluenemeta-sulphamide. An experiment which I undertook afterwards convinced me conclusively of the correctness of my view.

Equal portions of pure tolueneparasulphamide (fusing at 136°) and pure tolueneorthosulphamide (fusing at 153°–154°) were dissolved in water and subjected to fractional crystallization. Neither of these amides could be separated from the other, but constant fusing points were noticed indicating a tendency to crystallize together. I noted the fusing points 120° and 108° as the most stable. The mixed amide fusing at 120° crystallized in long, fine needles, while the mixed amide fusing at 108° crystallized in needles and small leaves; for the latter Beckurts gives a similar statement. Slight impurities lower the fusing point to 104°–105°, or even below that.

In conclusion I would state that Beckurts's toluenemeta-sulphamide fusing at 104°–105° was found to be a mixture of tolueneparasulphamide and tolueneorthosulphamide. This corresponds with the oxidation phenomena and its formation from pure tolueneparasulphamide and tolueneorthosulphamide.

The amide fusing at 186°–187° was found to be identical with Blomstrand's  $\alpha$ -toluenedisulphamide. The occurrence of toluenedisulphonic acid in the crude mixture, resulting from the action of fuming sulphuric acid upon toluene, is interesting in this respect. It was shown by C. Senhofer\* that the introduction of a second sulphy-group into toluene presents difficulties, and that only a mixture of anhydrous phosphoric acid and fuming sulphuric acid accomplishes this result satisfactorily. C. W. Blomstrand†, who undertook a similar investigation, heated toluene with fuming sulphuric acid at 160°, and obtained two different toluenedisulphonic acids, of which

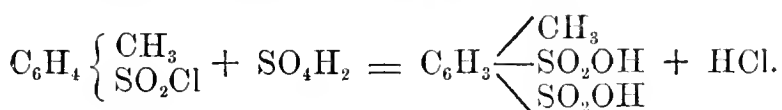
\*Ann. der Chemie, 164, 126.

†Ber. d. chem. Gesell., 5, 1084.

neither was identical with the acid obtained by C. Senhofer. It is difficult to say how the toluenedisulphamide from the liquid toluenesulphochloride was overlooked. The only explanation would be that no one knew the properties of the toluenedisulphamide, there being no statements on that subject published. This  $\alpha$ -toluenedisulphamide is very soluble in an ammoniacal solution; it is therefore only found in the solution, and not with the separated toluenemonosulphamides when toluenesulphochloride is treated with an aqueous solution of ammonia, as in the usual formation of amides. It is a singular fact that the toluenedisulphochloride is found again with the liquid and not with the solid toluenesulphochloride, when the two are separated in the way described at the outset. According to Blomstrand's statement the  $\alpha$ -toluenedisulphochloride is a solid body fusing at  $51^{\circ}$ – $52^{\circ}$ . In the course of this investigation, however, it became apparent that not only  $\alpha$ -toluenedisulphochloride, but also tolueneparasulphochloride is soluble in the liquid tolueneorthosulphochloride at  $-15^{\circ}$ .

I am at present engaged in the oxidation of toluenedisulphamide, upon which I hope to report as soon as the investigation is concluded.  $\alpha$ -Toluenecyanide has also been prepared from  $\alpha$ -toluenesulphonate of potassium and potassium cyanide, and will be studied in connection with the oxidation of toluenedisulphamide. In preparing toluenedisulphamide I made use of a reaction by which from the solid toluenesulphochloride and concentrated or fuming sulphuric acid, toluenedisulphonic acid was readily obtained in almost theoretical quantity; this proved to be the same acid from which the amide fusing at  $186^{\circ}$ – $187^{\circ}$  was derived.

The method consists in heating both substances together, when the reaction takes place as follows:



It is possible that a third sulpho-group may be introduced in this way and that other aromatic compounds may give analogous results. This investigation, however, I shall postpone for the present.

## ON THE PRODUCTS OBTAINED BY THE NITRATION OF METACHLORSALICYLIC ACID.

BY EDGAR F. SMITH AND GERTRUDE K. PEIRCE.

Metachlorsalicylic acid was prepared by the introduction of a calculated amount of pure dry chlorine gas into an alcoholic solution of salicylic acid. From the dichlor-acid, which was invariably produced in rather large quantities, it was separated by means of the barium salt, the latter being much more soluble than the corresponding derivative of the above acid. Frequently glacial acetic acid was employed to dissolve the salicylic acid, but as in this case there was usually an abundance of decomposition products produced, alcohol was substituted for the same.

Metachlorsalicylic acid was first obtained by Huebner and Brenken,\* studied later by Rogers,† and also by one of us.‡ In a pure condition the acid forms beautiful, long, colorless needles, readily soluble in water. It fuses at 172°C.

The first notice we have observed regarding the nitration of this acid was that of Rogers.§ He obtained from it monochlorodinitrophenol and a nitro-acid fusing at 151°C. His mode of forming the latter derivative was to mix the chlor-salicylic acid with glacial acetic acid and to the warmed solution add small quantities of fuming nitric acid from time to time. When the solution had stood for some time and was cool, a rather large quantity of water was poured into it, causing the separation of the greater portion of the nitro-acid.

Our plan of nitration was simply to add small quantities of the metachlor-acid gradually to fuming nitric acid in a medium-sized flask—shaking the latter constantly to aid the solution, and finally applying a gentle heat upon a water-bath. To the cold nitric acid solution water was added. A light yellow-colored mass immediately separated and was filtered, washed

\*Ber. d. chem. Gesell. 6 (1873), 174.

†Inaugural Dissertation, Goettingen (1875).

‡Ber. d. chem. Gesell. 11 (1878), 1227.

§Dissertation.

imperfectly with cold water and then boiled with an aqueous solution of potassium carbonate. The solution, after filtration and evaporation, was permitted to stand for some time. Long, deep red colored needles rapidly appeared. These were filtered off and farther examined. For convenience we would designate this crystalline mass A. From the filtrate upon farther evaporation there separated a mass of dark red colored nodules which, for the time, we will consider as B.

#### *Examination of Product A.*

This portion was redissolved and recrystallized slowly from an aqueous solution. The same needles appeared, and by filtering these before the solution had cooled, again evaporating and allowing to cool, to our surprise there appeared quite a different salt, forming bundles, consisting of orange-colored needles. Both the latter and the long red-colored needles were recrystallized and subjected to farther examination.

*Salt crystallizing in long red Needles.\* — Analysis.*—.1691 grams salt, dried at  $130^{\circ}\text{C}$ , were placed in a platinum crucible, a few drops of concentrated sulphuric acid added and a gentle heat applied. The residual  $\text{K}_2\text{SO}_4 = .0264$  grams, which corresponded to 15.60 per cent. K. The salt does not possess water of crystallization. The calculated amount of K in potassium monochlordinitrophenol is 15.23 per cent. There was, therefore, no doubt as to the constitution of this compound.

The free acid derived from this salt crystallized from aqueous solutions in long yellow needles, which fused at  $80^{\circ}\text{C}$  and solidified again at  $69^{\circ}\text{C}$ . It is also identical with the phenol of Rogers (see above) and the alpha-monochlordinitrophenol of Faust and Saame.†

*Salt crystallizing in orange-colored Needles.—Water Determination.*—.1617 grams air-dried salt lost upon heating at  $140^{\circ}\text{C}$  for a number of hours .0168 grams  $\text{H}_2\text{O} = 10.39$  per cent.

$1\frac{1}{2}$  molecules water require 9.53 per cent.

*Potassium Determination.*—.1449 grams dried salt gave upon evaporation with sulphuric acid .0480 grams  $\text{K}_2\text{SO}_4 = 14.86$  per cent. K. From this analysis we observe that this salt too

\* Proceedings Am. Phil. Soc. June 21, 1878.

† Ann. der Chemie (1870), 7 Supplement Band, 174.

is a derivative of a monochlordinitrophenole. The formula would be  $C_6H_2Cl(NO_2)_2OK + 1\frac{1}{2}H_2O$ .

This salt is much more soluble than the red. The color of the latter is so intense as to obscure the yellow, which consequently is overlooked unless great care is exercised in the purification of the red-colored compound.

Upon mixing an aqueous solution of this yellow salt with dilute hydrochloric acid, the corresponding phenol separated in yellowish-colored masses, which were recrystallized repeatedly from aqueous solutions, when long orange-colored needles appeared. The fusing point of this acid remains constant at  $79^{\circ}$ – $80^{\circ}C$ . The point of solidification was at  $25^{\circ}C$ , considerably lower than that of the acid corresponding to the red salt. In cold water the acid is rather insoluble, readily dissolved on applying heat.

Another noticeable difference in the above described phenols is in the silver salts. The alphachlordinitrophenol yields a soluble silver salt crystallizing in long bright red colored needles; the isomeric compound just mentioned above one which separates in bronze-colored needles, possessing a marked metallic lustre.

As the second phenol was formed in small quantities it was almost impossible to subject it to as thorough investigation as would seem desirable. The material, however, which was examined was thoroughly pure, and as the same analytical results were repeatedly obtained, the conclusion is that it is another of the many compounds having this composition.

Analysis:

.512 grams substance gave .6210  $CO_2 = .1693 C = 33.06$  per cent. C; and

.062 grams  $H_2O = .0068 H = 1.32$  per cent. H.

Calculated, C = 33.00 per cent. and H = 1.37 per cent.

#### *Examination of Product B.*

The dark red nodular crystals constituting the second product obtained in the nitration were crystallized repeatedly from water. The salt continued to grow lighter in color and at the same time assumed a more sightly form — presenting long, light yellow-colored needles, aggregating in fan-like masses with a satiny lustre.

The acid derived from this salt was light yellow in color, forming rather short, strong needles, exhibiting light refraction. When pure the constant melting point was discovered to be 162°–163°C. Very readily soluble in water.

Undoubtedly this is the acid described some years ago by Huebner.\* Rogers, too, probably had it in an impure condition. He mentions in his dissertation that he obtained an acid fusing at 168°C, and inferred that it was a probable isomer of the monochlornitrosalicylic acid which principally engaged his attention. Yet throughout our entire work we never discovered the slightest trace of an acid with a fusing point of 151°C. Our impure acid frequently fused about this temperature, but one or two recrystallizations were invariably sufficient to raise it to 162°–163°C.

Nothing more was done with the acid. Our attention was now directed to the formation of a few derivatives with a view of ascertaining how widely they differed from those of the supposed isomeric acid of Rogers.

*Potassium Metachlornitrosalicylate.* —  $C_6H_2Cl^mOH^oNO_2COOK$ .

Obtained by boiling the acid with a slight excess of potassium carbonate. Repeated recrystallization gave us the pure salt in aggregated needles with a beautiful satiny lustre. The salt yields a very bitter, disagreeable taste when placed upon the tongue. Very soluble in water. It is anhydrous.

*Potassium Determination.*—0.4872 grams of thoroughly dried salt treated with sulphuric acid gave, upon evaporation, 0.1623 grams potassium sulphate = 14.95 per cent. K.

Calculated, 15.34 per cent. K.

*Barium Metachlornitrosalicylate.*— $(C_6H_2Cl^mOH^oNO_2COO)_2Ba$ .

By boiling the aqueous solution of the acid with an excess of barium carbonate the salt was formed and crystallized in dark orange-red colored needles, which were very insoluble and exceedingly difficult to obtain pure. It appears to have water of crystallization, but on drying in the air rapidly loses the same. An analysis was made of the dried material.

\* Jahresbericht (1866), 349.

*Barium Estimation.*—0.2808 grams salt gave with sulphuric acid .1188 grams  $\text{BaSO}_4 = 24.70$  per cent. Ba.

Calculated, 24.03 per cent.

The silver salt formed a light brown colored powder, which was placed in a tube of Bohemian glass, an excess of ethyl bromide added, the tube sealed and heated for several hours in a water-bath, and in this manner we obtained

*Ethyl Metachlornitrosalicylate*,  $\text{C}_6\text{H}_2\text{Cl}^m\text{OH}^\circ\text{NO}_2\text{COOC}_2\text{H}_5$ ,

which, when crystallized from an alcoholic solution, formed almost colorless flattened needles, fusing at  $89^\circ\text{C}$ . A very strong light refraction was shown by the crystals.

Upon heating a portion of the ether with an excess of alcoholic ammonia we obtained

*Metachlornitrosalicylamide*,  $\text{C}_6\text{H}_2\text{Cl}^m\text{OH}^\circ\text{NO}_2\text{CONH}_2$ ,

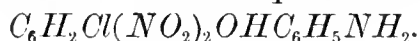
a brick-red colored compound forming small nodular crystals readily soluble in alcohol, more difficultly soluble in water. The fusing point is constant at  $199^\circ\text{C}$ .

Upon comparison with Rogers' work it will be found that our results are quite different, and this would indicate that two nitro-acids are formed when metachlorsalicylic acid is nitrated.

Our work in this direction has been discontinued, inasmuch as we have received information that the investigation of the acid has been almost completed by another party.

Another interesting compound which was obtained by us is the following combination of alpha-monochlordinitrophenol with aniline:

*Alpha-Monochlordinitrophenol Aniline.*



By mixing a small quantity of the phenol with sufficient aniline to dissolve the former in the cold, a beautiful deep red colored liquid was procured. A drop of this solution placed upon the skin imparted to the latter a rather difficultly removable stain. On evaporating the colored liquid upon a water-bath in a large open dish and allowing the same to cool, hard

nodular crystals separated, which were well pressed between paper and dried by exposure to the air. From aqueous solutions the compound is obtained in long, curled, light yellow colored masses. It fused constantly at  $137^{\circ}\text{C}$ . Aniline will separate upon boiling its aqueous solutions violently. An analysis of the substance showed it to be a union of one molecule phenol with an equal amount of aniline.

*Analysis*.—0.1221 grams dried substance burned with lead chromate gave .0188 grams carbon = 46.19 per cent. C, and 4.00 per cent. H. The theoretical percentages required are 46.22 per cent. C and 3.21 per cent. H.

UNIVERSITY OF PENNSYLVANIA, May 3d, 1879.

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## ON GLYCOCHOLIC ETHER.

BY ALFRED SPRINGER.

While engaged in experiments upon different ethers, it occurred to me that those of the acids commonly contained in bile, especially glycocholic and taurocholic, might be interesting. Since ox-gall is easily obtained, and its composition is tolerably well known, I chose that for my starting point.

At a first glance it would seem as if the etherification need require but little labor or time; nevertheless, any one who has ever experimented upon these acids can readily understand the difficulties which must be surmounted in order to avoid working with their decomposition products.

My first attempt at the preparation of glycocholic ether was as follows: After having extracted a quantity of sodium glycocholate from about twenty ox-galls, this salt was taken with a sufficient quantity of sulphuric acid and alcohol and distilled in a small glass retort. Only ethylic ether and alcohol passed over into the condenser. In the retort there remained a brownish-yellow resinous substance, insoluble in water and but partly soluble in alcohol or ether, which I found

upon examination to consist mainly of dyslysin mixed with choloidic and cholonic acids. A similar experiment made with hydrochloric instead of sulphuric acid gave equally unsatisfactory results.

I next prepared an alcoholic solution of the sodium salt, and passed dry hydrochloric acid through it for twenty-four hours, but still could obtain no ether. After this I placed in two strong glass tubes mixtures of hydrochloric and sulphuric acids respectively with alcohol and the sodium glycocholate, sealed them hermetically, and heated for four days on the water-bath. A thick resinous mass was formed, which again proved to be mainly dyslysin.

It is not unfrequently the case that an acid as such has a much greater affinity for etherification than a salt wherefrom the acid is liberated during the process. I have often observed that butyric ether made from sodium butyrate has neither so pure an odor nor taste as that prepared from butyric acid directly, although the same salt had been used as the starting point for both preparations. The same thing holds true with valeric ether also. These facts led me to try glycocholic acid in an isolated state instead of the salt with which I had been working.

Eighty ox-galls, fresh from the gall-bladder, were evaporated almost to dryness on the water-bath, and the residue was exhausted with alcohol. The alcohol was next distilled off, and the substance remaining in the retort was diluted with water and treated with milk of lime. To the filtered and cooled liquid, which had a faint wine color, dilute sulphuric acid was added until a permanent turbidity was produced. Soon the solution solidified forming a mass of crystals, which were again dissolved in water and the process of purification repeated. At last I obtained nearly a pound and a half of beautiful white needles of glycocholic acid.

These crystals, distilled with alcohol and sulphuric acid, showed no more inclination to form an ether than the sodium salt. But when they were heated with hydrochloric acid and alcohol in a sealed tube, an ether began drop by drop to form; until at the end of two weeks all the crystals had disappeared, and the ether collected upon the surface of the liquid in their stead. Later I discovered that this ether could be obtained more easily if the glycocholic acid was first dis-

solved in alcohol and dry hydrochloric acid passed twenty-four hours through the solution. This solution, heated in a sealed tube with alcohol and hydrochloric acid, became thoroughly etherified in two days. As the pressure within the tube was enormous, the usual precautions had to be taken against the danger of explosion. Since the ether was lighter than the other liquids in the tube it was easily taken off from the top.

The color of the ether is dark brown. Thinking that decolorization might be possible I tried to distill the substance, but found that it decomposed. Its specific gravity is 0.901. When exposed to the open air it decomposes, leaving a white resinous mass. In a closed vessel it may be kept for any length of time, and in a sealed tube it may be heated to a quite high temperature without suffering decomposition. Water acts upon this ether somewhat strangely. At first the mixture becomes thick and brown, as if it were dyslysin; but gradually it whitens, and crystals of glycocholic acid are deposited. The only way the ether could be washed was with hydrochloric or sulphuric acid.

During my experiments eighteen combustions were made of this ether and its educts. I need give the results of only one analysis. The nitrogen was determined by Constance Makris's modification of the Will-Vanentrapp process; a method which gave me extremely satisfactory results. The figures obtained agree very well with the formula  $C_{26}H_{42}(C_2H_5)NO_6$ .

		Theory.	Found.
Nitrogen,	...	2.84	2.89
Carbon,	...	68.15	67.23
Hydrogen,	...	9.53	9.40
Oxygen, by difference,	...	19.48	20.48
		<hr/> 100.00	<hr/> 100.00

Since the foregoing was written I have prepared several new ethers, namely, choloidic ether from ox-gall, and hyoglycocholic and hyotaurocholic ethers from pig-gall. I have these ethers in a pure condition, and have determined some of their reactions; but I prefer not to publish any detailed account of them until I have completed my analyses and definitely ascertained their formulæ.

REVIEWS AND REPORTS.

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## BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

*(Continued from page 66.)**Metallurgy — Continued.*

*Nickel and Cobalt.*—Within a decade the extraction of these metals has increased notably in importance; and the scale upon which they are worked has expanded greatly in consequence of their successful application in electroplating, while formerly nickel was scarcely used save in its alloys of the German-silver class, and metallic cobalt was not in industrial use at all. Extensive search has been made in various countries for new supplies of ore, in the main resulting in bringing together small lots from different sources. Probably the most important single new locality is New Caledonia, furnishing, not the more common sulphides and arsenides, but the hydrous silicate of nickel and magnesium known as Garnierite or Noumeite. The metallurgical processes in use are carried out partly in the “dry” and partly in the “wet way.” In the former direction there has been improvement, the result of experience, in the concentration of poor ores, such as nickeliferous pyrites, to mattes containing a much increased percentage of nickel, and the cobalt which may be present can be recovered in the state of oxide, to be subsequently reduced to metal, instead of obtaining it merely in the form of crude silicate, as “smalt” or “zaffre.” The metallic nickel furnished to commerce is of higher purity than was known a few years ago, 98 or 99 per cent. of real nickel being easily obtainable, and even higher grades of product seen to some extent. Moreover, the small, irregular grains and the cubes of but half-melted nickel which not long ago constituted the only forms in which the metal was turned out, have been largely replaced by solid ingots of various weights up to 5 or 6 kilos each, cast from crucibles in which, with the aid of well-arranged wind furnaces, the refractory metal has been completely fused.

*Zinc.*—The most noteworthy increase in the production of zinc of late years has occurred in the United States (New Jersey, Pennsylvania, Virginia, Tennessee, Illinois, Iowa, Wisconsin, Missouri), which may now be reckoned among the great sources of the world's supply.

The methods now and for a long time in use for the extraction of this metal from its ores still leave much to be desired; the various forms of distilling apparatus are complicated, more or less troublesome, and not adapted to continuous working; and much zinc is obtained as oxide by the burning of the metallic vapor in contact with air, or is deposited in a pulverulent form by too sudden cooling instead of condensing to liquid metal fit for casting into ingots. None of the attempts which from time to time have been made to devise a furnace capable of turning out, without serious loss, fused zinc by a continuous process, seem yet to have achieved success. The nearest approach to such success has been the continuous reduction and distillation of the metal with intentional combustion of the vapor, to produce zinc white for painter's use. It may possibly be worth consideration and experiment whether the volatilization of zinc might not be, at least to a large extent, prevented by reducing, under suitable conditions of temperature and furnace atmosphere, its ores along with those of lead, taking advantage of the fact, illustrated by the ancient method of making brass from copper heated with calamine and charcoal, that the presence of the less volatile metal in the alloy reduces notably\* the volatility of the other; the subsequent separation of zinc and lead admitting of being effected, as far as much the larger portion of each metal is concerned, by liqutation, as in the now common Parkes' process for desilverization of lead. If such a reduction method could be given practical shape, any zinc vapor which did still escape might be allowed to burn and collected as zinc oxide for painting.

*Tin.*—The most prominent fact for some time past in the history of this metal has been the very large addition to our annual supplies since 1870 coming from Australia, while the product from the Dutch East Indies has also largely increased. The tin-bearing territory of New South Wales and Queensland covers several thousand square miles, affording already some ore from veins likely to be much more largely opened up in the future, but much larger quantities from magnificent washings of stream tin. Tasmania also affords some smaller additional supply. Most of the Malay tin of Banca, Billiton, the peninsula of Malacca, &c., comes from "dry diggings" in decomposed granite or pegmatite, the more or less disintegrated remains of felspar and quartz being washed away, and the ore smelted on the spot in rude furnaces of small size with charcoal fuel, and a blast from the hollow trunk of a tree in which a piston works to and fro. Twelve or fifteen years ago the general supply of the world might have been set down in round numbers as—

\* It would have to be determined by experiment how far lead can thus give fixity to zinc at the temperature necessary for the reduction of both and separation of slag.

	Metallic Tin.
From England (Cornwall and Devonshire).....	8,500 tons.
“ Malacca and the Malay Islands.....	7,500 “
“ Saxony, Bohemia, and all other sources..	450 “
	<hr/> 16,450 tons.

A similar estimate for the present time stands thus:

From Malacca and the Malay Islands.....	14,500 tons.
“ Australia .....	10,000 “
“ England (Cornwall and Devonshire) ...	9,500 “
“ Saxony, Bohemia, Bolivia, &c., &c.....	650 “
	<hr/> 34,650 tons.

This doubling of production has been attended with a corresponding fall in price—from £127 to £61 per ton.

There has been no material change in the simple processes of tin-smelting. The application of Oxland's method of preparing the ore by getting rid of accompanying wolfram in the form of sodium tungstate has furnished some material for the utilization of tungsten compounds; most of the latter, however, so far as in use at all, are obtained from independently mined or mechanically separated wolfram.

*Bismuth.*—At the chief seats of bismuth production in Saxony and Bohemia, the old and simple process of extraction of the native metal from rock through which it is disseminated, by liquation in slightly inclined cast-iron tubes, has been abandoned, it being found that too much of the now quite valuable metal was left in the residues of imperfectly exhausted gangue. Instead, the mixed ores, largely associated with those of cobalt, are roasted and then reduced in the furnaces of the smalt-works with additions of charcoal, metallic iron and slag. Two layers separate after fusion, the upper one consisting of cobalt-speiss (arsenides of cobalt, nickel and iron), the lower of crude metallic bismuth. The latter is run off in the still fluid state after the former has solidified, and the bismuth, cast into blocks, is refined by eliquation at a gentle heat on an inclined iron plate. Almost pure bismuth flows off, while the foreign metals with a little bismuth remain as dross to be worked over.

To a limited extent the ores of this metal have of late years also been worked in the wet way—as at Meymac in France, where a small supply of oxidized ore is treated by solution in hydrochloric acid and precipitation by water or on bars of iron.

There has been a remarkable increase of demand for bismuth within a few years, leading to increase of price,

since although supplies of ore have been received from several new quarters, chiefly Peru and South Australia, in less quantity from Mexico, France, &c., the aggregate of these new receipts has borne but a small proportion to the amount furnished by the one long known and most important mining region of the Erzgebirge, of which Schneeberg in Saxony and Joachimsthal in Bohemia may be considered the two chief points. At present the annual supply is estimated as —

From Saxony and Bohemia,	. . . . .	32 tons
From all other sources,	. . . . .	3 “
		—
		35 tons

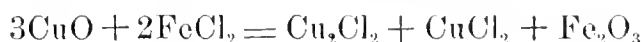
of which much the largest part is devoted to the production of bismuth oxychloride and hydrato-nitrate for use in medicine and as cosmetics, most of the rest being employed in making readily fusible alloys and producing the shell-like lustre on porcelain which has given rise to the name “porcelaine nacre.”

*Copper.*—Amongst the countries which have added most to the general supply of copper for the last quarter of a century are Chili and South Australia; the mines of the former have of late increased, those of the latter diminished in productiveness. To these will probably ere long deserve to be added Arizona, where valuable ores are abundant, and possibly at some later day Northwestern Texas. The product of the Lake Superior region has assumed an important place.

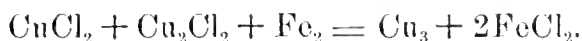
The general course of copper-smelting has undergone no great change for a long time, though there have been local variations of practice, due chiefly to special supplies of ore requiring particular treatment, and to the establishment of new seats of the industry. Swansea no longer fully holds the position of supremacy it formerly enjoyed, but the tendency is still marked toward the concentration of ores, and, of late years, of mattes and crudely smelted regulus of copper, at this and a moderate number of other centres, there to be treated with all the advantages of skilled labor, suitable and abundant fuel, &c. The most remarkable proposal of a new method of furnace treatment is that of Mr. Hollway, very recently brought before the Society of Arts of London, looking to the application of the Bessemer blast of air to sulphides in a melted state, the temperature being maintained simply by addition of fresh quantities of ore. Too little is yet known of the results even of such experiments as have been made for an opinion to be formed of the probable value of the idea; some advantages at once suggest themselves, but there are also manifest difficulties, such as the effect of the presence of much silica and the risk of loss by volatilization.

Relatively, much greater extension of processes in the liquid way has occurred of late years than has characterized the furnace methods. The very large use now made of the sulphur of more or less cupriferous pyrites in the manufacture of sulphuric acid has furnished abundant material, and the saving of the copper contained in burnt pyrites residues has become a regular subsidiary industry, especially in England, where in 1875 no less than 9600 tons of the metal were thus produced, several thousand pounds' worth of silver and gold being also obtained from the same source. The main features of the process consist in calcination of the spent pyrites mixed with common salt in furnaces often heated by gaseous fuel from a Siemens generator, leaching with water, and precipitation by metallic iron, preferably used in the spongy state obtained by reduction of some of the exhausted pyrites in a muffle furnace with ground coke.

In the United States the introduction of the Hunt and Douglas wet process should be particularly noticed — its wide range of applicability to ores of different kinds is one of its prominent merits. The material to be treated, roasted at a gentle heat if necessary to remove sulphur or decompose carbonate, is exposed to the action of a mixed solution of ferrous chloride and sodium sulphate and chloride,\* this being used either cold, or, with a view to more rapid effect, in a heated state; the undissolved residue is washed with a further portion of the same solution (hot); and from the mixed liquids obtained the copper is thrown down by metallic iron, reproducing the original solvent to be used over again. Taking only the case of the copper present as cupric oxide in the roasted ore, the reactions are essentially,



the cupric chloride dissolving of course in the water used, while the cuprous chloride is rendered soluble by the presence in the liquid of ferrous and sodium chlorides, and



This method has been successfully used with copper ores (simply), both of the oxidized and sulphurous classes, and also with ores containing the precious metals, these latter being obtainable from the residues after the copper has been removed by leaching.

The more careful examination which submarine telegraphs have led to of the great influence upon the conducting power of copper wire for electricity of impurities occurring to even a very minute extent, has stimulated the production of much

\* Obtained by the addition of common salt in excess to solution of ferrous sulphate.

purser copper than could readily be had ten or twenty years ago, and hence copper refining has assumed an increased degree of importance and commands increased attention and care.

*Lead.*—Among the greatest recent additions to the sources of supply of this metal must be counted the argentiferous and auriferous lead ores of the Rocky Mountains and outlying ranges to the eastward of the Sierra Nevada, especially in Colorado, Utah and Nevada, where galena and cerussite have been discovered and worked upon the grandest scale, the precious metals present often causing the lead to assume but secondary importance, while in the aggregate this latter possesses immense value. The same regions, speaking broadly, afford also vast quantities of iron and copper pyrites, and zinc blende; from the working of these for gold and silver much copper is saved, chiefly in mattes to be worked over elsewhere, while the great bulk of the zinc is lost.

In connection with the working of these ores, though of course applicable to and in practice applied to those of various other kinds, may be noted as capital improvements in mechanical treatment the use of the "Blake Crusher," the invention of Eli W. Blake of New Haven, Conn., for breaking down the ore to small fragments, the steady mastication effected by which is in marked contrast with the slow and power-consuming work of the old-fashioned crushing rolls; as also the substitution, for reduction of the crushed ore to powder, of stamp batteries made wholly of iron, with well proportioned and well finished parts, for the more clumsy constructions, partly of wood, which were formerly in use. Direct-acting, steam-driven stamps have also been brought into use, but to no large extent on account of their greater liability to need repairs at the hand of the skilled machinist, not always available in rough mining regions. Many valuable contrivances for the dressing and concentration of ores have also been added to the older arrangements.

In the chemical treatment of lead, as well as other ores, improved forms of roasting furnaces have proved of much value, particularly those of the type represented by the Gerstenhøfer and Stetefeldt furnaces, in which finely pulverized ore is fed in at the top of a red-hot shaft of fire-brick, down which it drops, encountering on the way an upward current of highly heated gases, partly the products of combustion from the fireplaces, but including an abundant supply of surplus atmospheric oxygen. These more modern furnaces have in a measure taken the place of the simple reverberatory for roasting, while for smelting the roasted ore this latter has also to a considerable extent been supplanted by small blast furnaces, in the construction of which hollow cast-iron walls traversed by a current of water—water-jackets—are coming into more

general use than formerly, replacing the fire-brick linings, which in some regions are procurable only from a distance and at heavy cost. The very general introduction of processes for desilverization, although of primary consequence in relation to the saving of the precious metal, has resulted also indirectly in softening and improving the character of the average lead of commerce.

*Mercury.*—As regards the supply of this metal, for which the demand has been greatly extended by the expansion of gold and silver mining within the last thirty years, the great fact has been the discovery of Californian cinnabar\* upon a scale placing the United States first amongst the countries producing mercury, while not inconsiderable though irregular supplies have also been received from Borneo. The present annual production may be set down in round numbers as—

From California.....	2353 tons (of 2240 lbs).
“ Spain (Almaden).....	1424 “
“ Austria (Idria) .....	273 “
“ all other sources.....	263 “
<hr/>	
4323 tons.	

The metallurgy of mercury still continues in a very unsatisfactory condition, the loss being enormous, while the low price at which alone the metal can now be sold ought to prove a stimulus to more economical management of the reduction. At present it is estimated that the best results are obtained at Idria, where nevertheless the loss is 30 per cent. on the amount of metal shown by assay to be present; in California there is an average loss of something like 40 per cent., while at Almaden in Spain it is set down as 50 to 53 per cent. To this immense waste must be added the large quantities afterwards lost in use, gold and silver amalgamation processes involving the sweeping down to the rivers of very much finely-divided mercury and its compounds, never to be recovered by any practically available means.

The chief sources of loss in reduction are, first, imperfect heating of the larger fragments of cinnabar-bearing rock, so that portions of ore remain unacted on in the interior; and, second, imperfect condensation of the vapor, which escapes from cracks and defective joints of the furnaces and passes through the porous masonry of their walls. The latter of these causes of loss is the more serious in the extent of its results. Attempts to obviate it, such as that made many years ago in the Palatinate under the direction of the late Dr. Ure, by

\* Cinnabar, accompanied as usual by small quantities of native mercury, occurs at sundry points not only in California, but northwards in Oregon, Washington Territory and Idaho. The deposits which up to the present have proved practically important are confined to the first named State.

using vapor-tight retorts of cast-iron heated from the outside and retaining the sulphur by means of lime, involve increased difficulty from the first mentioned cause, since the heat has to penetrate the semi-diameter of the retort as a whole, and the volume of material heated is swollen by the addition of the lime, while no heat is obtained from the combustion of the sulphur. The same remarks apply to the bell-furnaces of Bohemia, in which reduction is effected by means of iron or "Hammerschlag." Using such arrangements with poor ores—and the great mass of the ores usually available are poor—the consumption of fuel is extravagantly large, and the iron vessels are rapidly destroyed, or much cinnabar escapes reduction. In the brick-work furnaces used at all the most important seats of mercury production the sulphur is burned off by the oxygen of the air, producing much of the necessary heat, though Californian experience seems to have shown that there may be an unwise economy of outside fuel, it being well to supply by means of such fuel burned in separate fireplaces adjoining the hearth space occupied by the ore, ample heat to ensure the thorough expulsion from the rock of all mercuric sulphide. The great difficulty, however, arises from the escape of uncondensed vapor of mercury, the masonry and the underlying soil bearing ample testimony to this in the large quantities—thousands of pounds sometimes—of irregularly condensed metal found soaking through the porous material when old furnaces are taken down.

The most hopeful line of improvement seems to be that of a combination of all the safeguards which have individually proved more or less efficacious, along with perhaps some others which may be suggested, small in themselves, but likely to prove useful in detail, say some such general arrangement as the following: 1st, detached fireplaces, with grates adapted to the combustion of the fuel used, delivering their gaseous products of combustion into — 2d, hearths for the reception of the properly piled ore, to be constructed of an outer shell of cast-iron plates put together with planed flanges and screw bolts, or else of heavy riveted boiler-plate, made as vapor-tight as possible, with a thick interior lining of fire-brick; 3d, a first set of condensing flues leading from the hearths, also of heavy cast-iron, brick-lined only so far as the high temperature extends, with sufficient number of such flues and subdivision of cross-section to give extensive cooling surface; 4th, a second set of flues, extensions of the first, of stout Russia sheet iron, well asphalted inside and out by immersion at a temperature just short of redness in boiled coal tar, to resist the corrosive effect of the sulphur acids formed; 5th, a system of pipes for the injection of cold water spray into the condensing flues, and well-arranged drip-pipes to carry off *promptly* liquid water and condensed mercury; 6th,

an effective exhauster to produce forced draught through the flues irrespective of the temperature within them, and to prevent the tension of the contained gases ever exceeding the atmospheric pressure without. The same set of condensers might be worked with several fireplaces and hearths if intermittent firing be practiced, but with detached fireplaces it does not seem difficult to provide for continuous working by means of well-fitted and vapor-tight doors to the hearths for the discharge of burnt out ore and the introduction of fresh.

*Silver.*—In this country it is needless to more than refer to the immense additions to the world's stock of silver which Nevada, Colorado and other far Western States have made within twenty years, treasure comparable with and even exceeding the flood-tide from Spanish America in its period of greatest prosperity. In Europe the importance of the results obtained and their influence on present problems of finance and political economy, seem scarcely to be well understood by the general public, though no doubt familiarly known to many of those who concern themselves about such questions.

In various mining districts of the world, but notably in this region of new and great activity in the United States, there have been modifications in all three of the classes into which the processes for reducing silver from its ores may be divided.

1. *Amalgamation processes, involving the collection of the silver, however first reduced, by solution in mercury.*

Certain ores are found to be adapted to immediate amalgamation, while others cannot be thus profitably worked unless first roasted, either alone or more usually with an addition of common salt in order to produce silver chloride. For the purpose of this roasting, as with other like objects in view in the treatment of the ores of other metals above alluded to, new forms of furnaces, such as the Stetefeldt, have come into use, and have to a large extent replaced the time-honored reverberatory. The rotating hearth, as in Brueckner's furnace, providing for constant stirring of the material treated and the exposure of new surfaces to the hot gases and air from the fireplace, has in some hands given valuable results in application to this preliminary roasting.

For the amalgamation itself the classical Freiberg process, carried out in revolving wooden barrels, is no longer in use at Freiberg itself, having been given up a few years ago; it is still employed elsewhere, however, as in Chili, and up to a short time ago, at least, at a few works in the United States. The ancient Mexican or *patio* process, the invention of Fray Bartolomé de Medina in 1557, still holds sway throughout most of Spanish America. Its place has been taken in this country by the introduction within a few years of the so-called "Washoe" process of amalgamation in cast-iron pans. These shallow cylindrical or slightly conical pans may be considered as improved

forms of the old-fashioned Chilian mill or "arastra," replacing the clumsy blocks of stone dragged round in a stone trough by mules or oxen, by a machine entirely of iron, having well-proportioned scrubbers or mullers shod with easily removable plates of chilled iron revolving upon similar plates set in the bottom of the pan, and provided with the means of adjusting the distance between the grinding surfaces. Sometimes the bottom of the pan is steam-jacketed in order to permit heating the charge during amalgamation.

Sometimes the only materials introduced are ore, water and mercury; in which case native silver is simply taken up into solution by the mercury, while the chloride, bromide and even sulphide of silver are more or less effectually decomposed by the iron of the pan and by the mercury itself, the reduced metal being then also dissolved to a fluid amalgam. At other works "chemicals" are added to the contents of the pan, these consisting mainly of cupric sulphate and common salt, essentially the same materials as have long been used, the former in the impure shape of "magistral," in the "patio" amalgamation. The ore is placed in the pan in the state of subdivision in which it comes from the stamps, but is more finely ground during the amalgamation, especially during the first part of the process. Transferred to a generally similar pan known as the separator, but with the addition of much more water, the pulp is stirred round and round until the amalgam separates at the bottom and the soluble matter and great mass of silicious and earthy material from the gangue can be washed away, the amalgam being then drained of fluid mercury (holding a little silver in solution), and heated in an iron retort to drive off the rest of the volatile metal. In this process, greatly improved as it is in contrast with patio amalgamation on the score of time and labor consumed,\* and in spite of the advantage gained by experience as to details in its application, there is still much room for further economy, the loss being large in absolute value of the precious metal, either not chemically separated from some of its compounds in the ore (imperfect reduction), or not mechanically separated as amalgam from the "tailings" which are washed away (imperfect collection). The value of the mercury also lost is in the aggregate important, some of it losing its metallic form, as it serves as the means of reducing the silver by taking up chlorine, sulphur, &c., some of it being as finely divided metal mechanically washed away.

2. *Smelting processes, involving the reduction of the silver by furnace means, and its collection in solid alloy with one of the baser metals, usually lead, sometimes in the first instance copper.*

The use of improved forms of furnace for both roasting and

\*As has been often pointed out, the patio process is applicable in regions where want of fuel forms an obstacle to the use of quicker methods.

smelting lead ores has been already alluded to, and their merits have been tested on a large scale in the treatment of the argentiferous sulphide and carbonate found in such abundance in some of the States in the far West. The further treatment of the "base bullion" or argentiferous lead produced, with a view to the separation of the silver, requires now to be noticed.

The original invention of Pattinson of Newcastle, patented in 1829, for desilverization of lead, depends upon fusion of the metal in somewhat large mass, slow cooling, and removal with perforated ladles of the lead crystals as they solidify, repeating the process several times with the re-fused crystals on the one hand, which become poorer and poorer in silver, and with the residual lead on the other, this increasing in value up to a certain point, when it is cupelled. This mode of working has of late been modified by Rozan, a jet of high-pressure steam being passed into the bath of melted metal, stirring it up and exposing fresh surfaces to the air, so as to promote the oxidation and removal as dross of antimony, copper, &c., while the steam, as it condenses, leads to more regular crystallization than attended the older method. Hydraulic cranes are used in transferring the lead, doing away with much of the arduous hand labor formerly required. The results are favorably reported.

To a large extent, however, for some years past the process known as that of Parkes has been substituted for the ingenious invention of Pattinson. Zinc is added (1-5 per cent.) to the melted lead to be desilverized, the temperature being raised above the fusing point of zinc, and the two metals are well mixed by agitation. A prolonged period of repose follows, extending to several hours, during which the temperature is allowed gradually to fall, so that the zinc separates out on the surface in solid form, carrying the silver with it. The zinc is removed and afterwards distilled off in flask-shaped retorts of plumbago ware, the residual silver being finally fused with a small quantity of lead and cupelled. This Parkes process has become well established in the United States, and has received here some useful improvements in the details of its application.

3. *Processes carried out in the liquid way, the silver, as one of its compounds, being brought into solution and afterwards precipitated.*

These methods have of late years received a moderate degree of extension, although their importance as regards aggregate result is trifling in comparison with amalgamation and smelting. The Ziervogel process, involving the production of silver sulphate by careful roasting of the ore without common salt, and extraction of this sulphate with hot water, has perhaps made more progress than chlorination by roasting

with salt, followed by washing out of silver chloride with brine or solution of sodium thio-sulphate. Experiments have been made in the United States with Plattner's chlorination by means of chlorine gas, followed by leaching to extract silver chloride, and also with Ziervogel's process combined with subsequent amalgamation of the washed residue.

*Gold.*—The great discoveries of gold in California and Australia, first in the form of sand and nuggets in river gravel, have proved important, not only in the wealth they have afforded within thirty years, and the movements of population and rapid extension of civilization they have given rise to, but in the stimulus given to study of the modes of occurrence of the precious metal and the best methods for its extraction. Not only have existing river-beds been explored, but vast masses of alluvium from water currents that have for ages ceased to flow are washed over, and by mechanical arrangements which, starting from the simple pan in the hands of the laborer in 1849, have culminated in the "hydraulic mining" of the present day, employing sometimes the force of a jet of water six inches in diameter, projected with the pressure due to a head of more than four hundred feet. Before long the attention of the seekers after gold washings was attracted to the veins of auriferous quartz, and gold diggers became gold miners; improvements were made in the mechanical appliances for crushing quartz upon a great scale, and in the amalgamation process for extracting the gold from it; this source of material having for years past grown in importance as the richer stream and dry alluvial works remaining have waned in number and extent. Finally the gold existing in microscopic or even ultra-microscopic particles distributed through masses of pyrites, galena, blende, carbonate of lead, &c., and associated with other ores, as of silver, has come into requisition, and ore by hundreds of thousands of tons is worked which does not contain on an average as much as .0001 of its weight of gold. Much of the ore from even the great "bonanza" of the Comstock lode might not many years ago have passed under the eye of an experienced miner without its containing useful metal of any sort being suspected. The only strongly-marked contrast to such material has been presented by the marvellously rich pockets and small veins of tellurides in Colorado, very limited in extent, but furnishing sometimes small lots of ore worth \$40,000 or \$50,000 a ton.

The defects, mechanical and chemical, of the processes in use for the extraction of gold lead to immense losses in absolute value, such as may be counted by millions of dollars annually. It has been estimated, by comparison of the results actually obtained on the large scale with those of careful assays, that quartz amalgamation involves a loss of 12 to 15 per cent. of the gold actually present, while probably still

poorer returns are obtained by "hydraulic" treatment of alluvial gravel, 15 to 30 per cent. of the gold *exposed* being supposed to be lost.

The methods for collecting by smelting the generally very small quantities of gold from pyritous ores and those of lead and zinc are essentially the same as in the case of silver, above alluded to, and the same progress has been made of late years; in fact both the precious metals are commonly obtained together in the matte or base bullion, from which the inferior metals are separated by the same operations. Although these smelting processes yield in the aggregate far less gold than is obtained by washing and amalgamation, there is reason to believe that it is obtained with a less proportion of loss.

The chlorination process of Plattner has been used to but a moderate extent. It demands very careful roasting of sulphurous ores as a preliminary step. The use of bromine, now obtainable at a very low price, seems worth attentive consideration, especially if combined, as it might be, with arrangements for recovering the bromine.

As regards the separation of gold and silver from each other, the long known method of "parting" by solution of the latter metal in acid is varied mainly as respects the kind of acid used, European practice having for the most part long since settled down upon hot, concentrated sulphuric acid, while at very large refining works in San Francisco local conditions some time ago caused nitric acid to be preferred, one of these conditions being understood to be the trouble there of disposing of sulphur dioxide economically without nuisance, while the lower oxides of nitrogen can be carried into the furnaces and their oxygen taken up by the fuel.\* The immense supply of "argent doré," as the bullion is called which the ores of the Comstock lode in Western Nevada yield by amalgamation, has for several years placed the San Francisco works on a most favorable footing for the application of the parting process, since the bullion contains on an average about 4.75 per cent. of gold by weight in proportion to silver, and therefore needs no addition of the latter metal to secure complete separation by the acid. When gold is the predominant metal, and it becomes necessary to dilute it by further alloy—the old process of "quartation"—in order to avoid cloaking and protection of the portion of the mass which the acid should dissolve, it has not long since been proposed to replace silver, which has hitherto been generally used as the diluting metal, by one of less value, and it has been shown that zinc, added to the extent of five to eight times the weight of the bullion

\* In San Francisco, in connection with the employment of sulphuric acid, precipitation of the silver sulphate by a hot, concentrated solution of ferrous sulphate, has been brought into use instead of the metallic copper precipitation.

to be treated, may be very easily alloyed with it at a comparatively low temperature, while nitric acid will afterwards readily dissolve out zinc, silver, copper, &c., leaving the gold fine. If this be brought into use on the large scale, the more costly nitric acid might in all probability be dispensed with by dissolving out the zinc first with diluted sulphuric acid, and then boiling the residual metallic sponge with the same acid in the concentrated state so as to take up the silver and copper.

Much merit attaches to the ingenious chlorine gas process, invented by Mr. F. B. Miller of the Sydney Mint, New South Wales, for separating the two precious metals when alloyed with gold in excess.\* He passes a stream of gaseous chlorine down into a crucible containing the alloy in a state of fusion until the silver is converted into chloride, decants this off, recovers a little gold from it by refusion with a small amount of sodium carbonate, and then, casting it into slabs, reduces to metallic silver by means of zinc and a little dilute sulphuric acid. This process, which has since its publication been applied in European refining works, is as well fitted for the special service of dealing on the spot with the large masses of Australian gold bullion, as the San Francisco "parting" is applicable to the silver bullion of Nevada.

*Platinum.*—The most important change in the method of working the refractory alloy which constitutes what is called native platinum has been the introduction of Deville's process for dealing with it by purely furnace means, avoiding the tedious and expensive solution in aqua regia, and separation by subsequent precipitation as originally proposed by Wollaston, and exclusively practiced since the beginning of the century. The main features of Deville's process consist of fusion with galena and litharge, separation of the osm-iridium left undissolved, cupellation of the platiniferous lead alloy obtained, and fusion of the residue left upon the cupellation hearth by means of a stream of ignited oxygen and hydrogen or coal gas in a furnace of compact lime. Although this method has been used upon the large scale, and much platinum has been worked by it, it is said to have lost favor with the principal manufacturers and to have already fallen out of use. The product obtained by it is not pure platinum,† but an alloy with iridium and rhodium mainly, better capable, it is true, than the pure metal of withstanding the action of acids and other chemical reagents, but harder, less freely malleable, and more troublesome to work mechanically. On the other hand, Deville un-

\* This process is also available as the means of toughening such gold as is occasionally found to be brittle and mechanically intractable from the presence of traces of certain of the baser metals, such as lead, antimony, bismuth, &c.

† Nearly, if not quite, all the platinum of commerce contains at least traces of iridium, but in the product of Deville's method of treatment iridium and rhodium occur in quantity varying from 2 or 3 to 25 per cent.

doubtedly deserves the credit of having given practical shape to the *fusion* of platinum in large masses, substituting this more perfect mode of producing compact ingots for the troublesome and less satisfactory *welding* which alone Wollaston had been able to employ. This feature of the new process has become thoroughly established, and will without doubt be permanently retained in use.

### *Metallic Alloys.*

Amongst the most interesting and valuable materials of this class which may be called new, or comparatively new, may fairly be named the following :

*Aluminum bronze*—a result of the experiments made by Deville upon an industrial scale with metallic aluminum, consists usually of about 90 per cent. copper (which should be of the greatest attainable purity) and 10 per cent. aluminum, although these proportions are subject to variation. It may therefore be looked upon as gun-metal in which tin has been replaced by aluminum. It is distinguished by a bright yellow color which may be made closely to imitate that of gold, by capability of resisting in a very high degree both tensile and compressive strains and abrasive friction, by rigidity and remarkable elasticity, while it readily furnishes sound castings and may be forged with satisfactory results.

*Phosphor-bronze*—a modified gun-metal, was first produced, and carefully tested on a large scale (after several earlier experiments looking in the same direction by others, as Abel in England and Ruolz in France), by Montefiore-Levy and Kuenzel of Belgium, in 1870-71. It consists of copper and tin, either in the proportions for ordinary gun-metal, viz. 90 per cent. copper and 10 per cent. tin, or, preferably, with an increase in the amount of the former and diminution of the latter metal, some of the best results being obtained with about 5 or 6 per cent. of tin, while in either case a little phosphorus is added. Of this last element, added in the form of a previously prepared phosphide of tin, a variable portion burns out during the fusion of the alloy, but a small amount is retained ranging from a small fraction of 1 per cent. up to a maximum of about 2 per cent. Its effect seems to be threefold, first to eliminate, by combining with, any oxygen which may exist in the copper-tin alloy,\* whether as oxide of one or both metals, or occluded in the free state, thus tending to increase and assure the homogeneity and compactness of the alloy; secondly, by supplying a more easily oxidizable element to prevent burning out of tin during the fusion and casting of the alloy, thus rendering the proportion between the two metals more definite

\* Phosphorus has also been very successfully used, as phosphide of copper, to aid in the removal of oxygen by the "poling" process for the production of refined and tough copper.

and permanent; and thirdly, so far as any phosphorus remains in combination in the alloy, to notably increase its hardness, the effect of even a very small proportion being comparable in this respect with the effect of combined carbon on iron in ordinary steel. The most prominent general properties of the alloy are great tensile strength (in some specimens an increase on that of ordinary bronze in the ratio of 5 to 2), rigidity, hardness, consequent resistance to abrasion, and elasticity. Results of a remarkable character were obtained in trials made, under the auspices of the Belgian Government, of this alloy as the material for field-artillery, although these results were not without drawbacks in regard to this special application. For portions of the machinery of powder mills, and for hand-tools used in such works and in powder magazines, for the cartridge-cases of breech-loading firearms, for pump-cylinders and the screw propellers of sea-going vessels, and with certain changes in the character of the alloy\* leading to the pretty uniform distribution of hard metal through a softer basis, for the bearings of shafts and other moving portions of machinery, this material has approved itself as of real value. Its general interest is very great, as opening up a field for investigation in regard to the steel-like modification of alloys of the softer metals.

*Manganese argentan or German silver.*—The very large consumption of the alloy of copper, nickel and zinc known as German silver, in reality a hardened and whitened brass, as the material for spoons, forks and other articles requiring mechanical strength and rigidity, to be afterwards plated over with silver, has of late years met with interference from the increasing rival demand for nickel to be itself galvanically deposited upon other metals, and a certain degree of importance attaches to the manufacture, at first experimentally by several persons, as Parkes of England and Montefiore-Levy and Kuenzel of Belgium, and since on an industrial scale, of a similar alloy in which nickel is replaced by manganese either wholly or in part, the following being some of the proportions used:

Copper .....	54.50	55.50	52.25	50.00
Manganese .....	25.50	13.00	22.25	5.00
Nickel .....	...	...	...	10.00
Zinc .....	20.00	31.50	25.50	35.00
	<hr/>	<hr/>	<hr/>	<hr/>
	100.	100.	100.	100.

\*Addition of lead, which causes segregation of the alloy on cooling into two portions, the one being a hard and tough phosphor-bronze containing very little lead, the other a much softer alloy, consisting chiefly of lead with a small proportion of tin and traces of copper. Railway axle-bearings on the Great Central Railway of Belgium wore out a kilogram of ordinary gun-metal for 99,900 kilometers run, while the same quantity of the phosphor-bronze and lead alloy was worn out for 429,200 kilometers.

Analogous alloys, to which tungsten is also added, have of late been made by Biermann of Hannover. The general character of such material enables it to be used instead of the ordinary German silver, although the hardening tendency of manganese is strongly marked, and unless properly regulated easily leads to trouble from cracking of the alloy in working. The increased tendency to oxidation seems also to call for attention.

*Iridio-platinum.*—The material finally agreed upon by the International Bureau of Standard Weights and Measures as that to be used in making the new and, it is hoped, permanent standards of weight and length, consists of 90 per cent. platinum and 10 per cent. iridium. It has been produced in masses of magnificent dimensions, one fusion, under the direction of Deville, having turned out 250 kilograms at a single operation, while Matthey, of the firm of Johnson and Matthey of London, has made rules for geodetic measurements, each of 4 meters in length by 21 millimeters wide and 5 mm. thick. The high density of the alloy—21.512 at zero—its malleability, coupled with a considerable degree of hardness, its rigidity and elasticity, capability of receiving a beautifully polished surface and sharp, delicate graduation lines, and its inalterability by any ordinary chemical exposure, all appear to fit it remarkably well for the use being made of it and to justify the choice of the International Bureau; yet it seems fairly to admit of question whether any alloy or any compound or mixture is to be preferred for such a purpose to an elementary metal, such as platinum, about whose homogeneity, uniformity of physical properties, and above all permanence of character, less doubt may well be entertained.

Our knowledge in regard to alloys in general has received valuable extension from the researches of Matthiessen,\* conducted more particularly with gold, silver, copper, tin and lead. It is greatly to be desired that his investigations, cut short by too early death, should be resumed, and carried forward with similar intelligence, accuracy, and desire for the discovery of general principles rather than of immediately applicable facts merely.

A recent (1876) observation of a general kind, and novel in itself, has been made by Prof. Silliman in regard to the possibility of conferring sonorous elasticity upon soft alloys, as of tin with antimony, copper, &c., such as "Britannia metal," by a peculiar method of tempering, articles cast from such alloys being immersed for a short time, from a few seconds to a minute or more, in a bath of paraffin oil or melted paraffin, heated to a temperature about 3° C. below the fusing point of the alloy, hence usually to 220°–230° C.

\* Brit. Assoc. Rep., 1863; Proc. Roy. Soc. xi. and xii.; Phil. Mag. xiii., &c. Some researches of general interest have lately been published by Roberts on alloys of silver and copper (Proc. Roy. Soc. xxiii), and by Riche on alloys of copper and tin (Ann. Chim. Phys. [iv.] xxx).

*Electro-Metallurgy, and other Alterations of Metallic Surfaces.*

The practical substitution, on an industrial scale, of dynamo-electric machines for galvanic batteries, in the production of the current needed for electroplating, as may now be witnessed in New York, and doubtless in other cities, is worth noting as one illustration of the more economical series of transformations of the potential energy of coal by which electricity is now made available for useful purposes. The simplicity of application, easily worked arrangements for varying the strength of the current and its adjustment to resistance, and several collateral advantages, as of cleanliness and durability, render these machines very satisfactory. It would be interesting to have a full report on the different forms in use for this particular purpose, with specifications of the first cost, expenditure of driving power, work done, &c.

To the three metals, the deposition of which has for forty years been the chief work accomplished by electro-metallurgy, — viz., copper, silver and gold — has now (since 1870) been fairly added a fourth in nickel, whose successful introduction we owe to Mr. Isaac Adams of Boston. His observation that double salts of nickel and *ammonium* afford solutions from which the metal may be readily thrown down as a coherent and lustrous film, forms the basis of the already important nickel-plating. The nearly white color of the metal, its hardness, superior to that of silver, its but slight tendency to tarnish or rust on exposure to oxygen, sulphur compounds, water, or other commonly occurring atmospheric substances, with its cheapness in comparison with silver or gold, combine to make it extremely valuable for a multitude of applications requiring the protection and concealment of iron, brass, copper and other of the baser metals. In tenacity, hardness, and resistance to chemical alteration, cobalt, which is deposited under like conditions, seems to stand upon nearly the same footing with nickel, while in color it is perhaps superior, being bluish rather than yellowish grey, and when polished presenting a nearer resemblance to silver. The sparing occurrence, however, of cobalt ores, and the large demand for cobalt oxide and silicate in connection with glass staining, porcelain painting, and the manufacture of pigments, tend to limit the scale upon which this metal can be used for plating.

Although the reproduction of engravings was among the first applications of electro-metallurgy, the rapid growth of this application, its expansion in new directions, and the immense extent to which for some years past it has been made serviceable in connection with printing, both of matter at first set up with movable type and of engraved work of the most various kinds, cannot be overlooked amongst novel features of modern industry. In this direction both forms of electro-

metallurgy are made useful; the superficial coating of one material with another, as in the harder surface given to ordinary type by the deposition of copper, nickel, and even occasionally iron; and the plastic reproduction of an engraving or a page of type, multiplying with wonderful rapidity and perfect accuracy the printing surfaces from which the myriad impressions upon paper are to be stricken off.

There still remain some applications of the electric deposition of metals obviously desirable but not yet satisfactorily made. One of these as yet unsolved problems seems to be the production of a really good calico-printing cylinder, of cheaper material than massive copper, and having the intaglio pattern accurately and rapidly transferred to the surface by electro-metallurgy. Improvements in the means of treating the existing cylinders, removing old patterns from them and replacing by new ones, have diminished the importance of this question, but it still remains worthy of examination.

With regard to other alterations of the surface of metals, partly mechanical and partly chemical, the last few years have seen continued and rapid extension of long known processes, such as the tinning of sheet iron, which has received the stimulus of enormous demand for the product arising from the employment of "canned" provisions on a scale far beyond that of even ten or fifteen years ago; the coating with zinc or so-called "galvanizing" of iron, which has been in considerable degree stimulated by the stretching forth of scores of thousands of miles of telegraph wire and the increasing use of iron roofing; the production of "malleable" iron castings for innumerable purposes, especially house fittings and builders' furniture, locks, hinges, and the like, the softening of which by superficial burning out of carbon is effected with noticeably greater success and uniformity than used to be attained; and the opposite manufacture of articles of forged iron "case-hardened" by superficial addition of carbon to form a steely coating, mechanics' tools of various sorts furnishing a wide field for the cheap and useful application of this alteration of surface.

Among the more novel industries of this sort may be mentioned the recently (1877) introduced process of Barff for protecting iron from rust by exposure to superheated steam at predetermined temperature and for a properly regulated time. The result is the coating over the surface with a very hard and closely adherent layer of magnetic oxide. That this general result is not in itself new is manifest, a thinner coating of the same sort having long been used for the same purpose, upon parts of fire-arms for instance, and the comparative exemption from rust of the black surface of iron bars from a rolling mill and fresh forged work from the blacksmith's hammer being due to the same cause. In this respect the

florid language used by sundry reporters of the supposed new invention is far from being justified. But real merit undoubtedly attaches to the special method by which the object in question is secured,\* and to the care with which the details seem to have been worked out. It is stated that if superheated steam at 500° F. be used, and the exposure of the articles to be protected be continued for five hours, a surface is obtained which will resist emery paper for a considerable time, and which will not rust within doors after any moderate degree of exposure to moisture; while, if the oxidizing process be conducted at 1200° F., and continued for six or seven hours, the surface will resist a rasp, and will bear prolonged exposure to the weather out of doors. The oxidation does not affect the appearance of the surface otherwise than by turning it black, the texture of the surface remaining unaltered, whether it be that of a rough forging, of a turned or a polished object.

There can be no doubt that for many purposes the protection against rust thus given the surface of iron will be valuable, and if the assertions made in regard to the thoroughly firm adhesion of the film of magnetic oxide, even under conditions of greatly and rapidly varied temperature, prove to be sustained, and the anticipations of the inventor of the process, that it may be applied to the plates of steam boilers, and of iron ships, be successfully carried out into practice, this may perhaps be ranked as one more of the not very numerous list of methods, of first-class importance, for usefully modifying the surface of worked metals.

J. W. MALLET.

[To be continued.]

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ANIMAL CHEMISTRY; OR, THE RELATIONS OF CHEMISTRY TO PHYSIOLOGY AND PATHOLOGY. By Charles Thomas Kingzett, F. C. S. London, 1878. Pp. 494.

The object with which this book was written is not at first quite obvious, since, in spite of its dedication to medical men and scientific chemists, it is clearly not suited for either; it is too full of uninteresting and, so far as we know at present, unimportant minutiae for the physician, and too meagre in technical details for the chemist, who will not find it in any degree adequate to replace the well-known manuals of Hoppe-Seyler or Gorup-Besanez. A little examination, however, serves to show without much doubt that the real object of Mr.

\*Mr. G. Bower has also experimented upon the production of a coating of magnetic oxide by exposure of the iron to heated air at regulated temperature, and by like exposure to air mixed with carbon dioxide (gaseous products of combustion), followed by a stream of carbon monoxide, which leads to ferric oxide being first formed, to be afterwards reduced to the magnetic oxide.

Kingzett's publication is the glorification of Thudichum; Allah-il-Allah — there is but one physiological chemist and Kingzett is his prophet. Gratitude in a pupil is an admirable trait, but it should be kept within bounds; which is hardly the case when it leads to the production of a manual in which the foremost living workers are ignored or sneered at, while the beloved teacher is not only constantly quoted for what he has done, but given as the authority for what he has not. The effect is, in truth, somewhat ludicrous when Thudichum is dragged forward as the sponsor for all sorts of opinions which have long been the commonplaces of the physician or physiologist. As examples, take the following:—"According to Thudichum, the spleen contains much blood"—"Thudichum points out that in leuco-cythemia the spleen is frequently large"—"Thudichum states it is probable that improper nutrition has the main share in causing these diseases (scrofula and tuberculosis) in many children."

A far more serious defect, however, is the author's entire ignorance of physiology, which crops to the surface in almost every page, and in reference to almost every subject. When he tells us that from Frerich's researches it would appear that Peyer's glands contribute but slightly to the formation of intestinal juice, it is pretty clear that he has no idea what a so-called Peyer's gland is. When he writes that "there can be no doubt that the principal function performed by the liver consists in the elaboration of bile and its secretion," he will find but few physiologists to agree with him. The statement that the colorless corpuscles of the blood are "constantly vibrating" proves pretty conclusively that he never saw the bodies he is writing about, while the researches of the last few years are altogether ignored in the statement that sweat is nothing more or less than a liquid exuded from the blood-vessels. We were rather of opinion that it has been satisfactorily proved that sweat, although its materials are derived from the blood, is in no way an exudation, but a true secretion formed by the gland-cells under the influence of certain nerve fibres. However, ignorance of comparatively recent work is more or less excusable; but when we come to the subject of respiration and find Mr. Kingzett still living mentally in the age of Lavoisier, we find an ignorance which is quite unpardonable, although one is perhaps inclined to be less severe on account of a feeling that the author is, after all, an object of pleasant antiquarian interest. If there is one question in animal chemistry which seems beyond dispute, it is that oxidation takes place no more in the lungs than elsewhere, in fact rather less; and nearly all are now agreed that the main oxidative processes in the body take place in the living tissues and not in the circulatory blood. But read the following extracts:

"Alcohol . . . a respiratory food, or a substance which ad-

mits of oxidation in the lungs," p. 153. "Modern researches tend to show that vitality consists more in changes occurring in the blood," p. 198. "The source of vital force, viz. blood oxidation," p. 181. It is true the contrary doctrine is referred to as held by various authorities, but several pages are given up to expounding with approval the views of a Dr. Hake, who seems to be an extreme supporter of the Lavoisian doctrine, and who holds that "the oxidation of carbon and hydrogen in the lesser circulation is (was) the source of muscular in common with all other vital force"; and again, that "the cerebro-spinal system does not generate its own force, but derives it through the chemical changes in the lungs." Further, Dr. Hake believes (p. 181) that the brain is a great storehouse of energy, whence it is transmitted to the muscles, glands and so on, and Mr. Kingzett seems to think this quite plausible. It is enough to make Haller turn in his grave to have his labors ignored in this way, and to find in the nineteenth century the nervous system spoken of as supplying the muscles with their contractility.

It would be a long task to point out the misstatements which meet us in every chapter. It is, however, only fair to Stokes to point out that he did not demonstrate that arterial blood gave a spectrum with two absorption bands while venous blood exhibits but one. Every physiologist knows that ordinary venous blood gives the two bands, and that the single band only appears in the blood of asphyxia.

We cannot conclude without quoting the description of the structure of the teeth, which will delight histologists:—"Indeed, the roots or stumps of the teeth are bones, properly so-called. The exposed parts of the teeth, however, consist of many minute tubes of peculiar construction, and composed of what is called dentine; over this there is a harder epithelium structure called cement."

In a preface the author states that the book was written to complete a connection with studies in physiological chemistry which had been attended for four years with unflinching success. We regret we cannot congratulate him on the success of his crowning effort. Should he again contemplate resuming such studies, we beg him first to learn a little physiology: he would probably be surprised to find how useful it would be to him.

H. NEWELL MARTIN.

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THE CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF STEEL RAILS. By Charles B. Dudley, Ph. D., Chemist of the Pennsylvania Railroad Company, Altoona, Pa.

This memoir was originally prepared as a report to the Pennsylvania Railroad Company, and has been since presented

to the American Institute of Mining Engineers and published in its Transactions. The paper is mainly devoted to an account of the chemical composition (as to C, Si, P, and Mn) and certain of the physical properties of twenty-five samples of steel rails, whose history has been recorded in reference to the positions they occupied on the road-bed, amount of tonnage which passed over them, extent of wear, giving way or not by fracture, &c. The work of examining these steel specimens seems to have been carried out with care, and the results, both as given in detail and as tabulated in condensed form, may be studied with much interest.

As regards the physical conditions involved, it is to be regretted that the tests made of tensile strength, elongation before rupture, angle of torsion, &c., seem to have been applied only to the worn and in some instances fractured rails which had been removed from the road and were submitted to analysis. It would have added much to the interest and practical value of these tests had they been also applied beforehand to the rails when new and as yet unused. It can hardly be supposed that the original character of a piece of steel was represented by its behavior under physical tests applied after it had been in service for ten years, and had endured the passage over it of 37,005,142 tons.

The chief point in the discussion of the chemical result which seems fairly open to criticism is the mode adopted of expressing the sum of the elements found (other than iron) in terms of what the author calls "phosphorus units"; .01 per cent. of phosphorus being taken as such a unit, and the assumption made that an equal effect in hardening steel and rendering it brittle is produced by .02 per cent. of silicon, .03 per cent. of carbon, and .05 per cent. of manganese, so that "the phosphorus units are found by adding together the phosphorus, one-half the silicon, one-third the carbon, and one-fifth the manganese, expressed in hundredths per cent." The author admits that he does not know of any definite relations having ever been discovered between these substances in this respect, and furnishes no reasons for his arbitrary assumption of the above figures, thus reducing the value of the conclusions he draws as to the united effect and distribution of effect of these ingredients. In view particularly of the great importance attaching to the influence of carbon and phosphorus respectively upon steel,\* and to the capability of in a sense mutual replacement which these ingredients seem to possess, it is desirable to obtain results as

\*The problem of sufficiently removing phosphorus from cast iron containing it in large quantity, so as to make good steel, alluded to in the April No. of this Journal, foot-note to p. 65, seems to have a chance of satisfactory solution in the experiments now being carried out upon a large scale by Messrs. Bolekow, Vaughan & Co. in England upon the application of the Bessemer process with lime-lined converting vessels to pig-iron made from Cleveland ore.

far as possible uncomplicated by assumptions like those just mentioned.

The value, however, of such experiments as the author has made lies mainly in the data which they afford for future comparison with such others as may hereafter be accumulated; and in the publication of the results of accurate quantitative measurements, chemical and physical, instead of more or less vague estimates merely of the character and behavior in service of steel for railroad use, Dr. Dudley has done good work. One of his conclusions calls for special attention and comparison with similar observations elsewhere, namely that some at least of the harder rails wore away more rapidly in service than those of softer steel. This is in accordance with certain results lately reached in England. In regard to this very important point, capability of withstanding abrasion, it seems by no means likely to be a matter of indifference whether the hardening of the metal be effected by carbon alone or mainly, chiefly by phosphorus, silicon, &c., or by several such elements present together in varying proportions.

J. W. M.

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FOREIGN PHOSPHATES. By Dr. Charles U. Shepard, Jr. Charleston, S. C. 1879.

This pamphlet, the report of a public lecture delivered to a popular audience, contains a useful survey of the world's chief sources of supply at present of the various materials — bones, recent and fossil; so-called coprolites; guanos and rock-guanos; mineral phosphorite, apatite, &c.—capable of yielding phosphoric acid for agricultural use. Its interest is increased by some details as to the principal European localities affording phosphates, the results of personal observation by the author on a recent visit to these deposits. The large veins of Spanish phosphorite, especially at Logrosan in Estremadura, the excellent quality of the material they afford, and the low price at which it may be furnished when legal injunctions now preventing work shall be removed, are spoken of in very high terms.

J. W. M.

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ELEMENTARY QUANTITATIVE ANALYSIS. By Alexander Classen, Professor in the Royal Polytechnic School of Aix-la-Chapelle. Translated by E. F. Smith, A. M., Ph. D., Assistant in Analytical Chemistry, University of Pennsylvania. Published by Henry C. Lea.

This work is constructed on the same plan as Woehler's *Mineral-Analyse in Beispielen*. It consists almost wholly of clear and specific directions for the analysis of particular compounds, alloys and mixtures, which have been selected as

examples to illustrate the best methods of quantitative determination and separation. These examples have been chosen with such excellent judgment that they involve a wide range and large variety of quantitative work, without being too numerous for the ordinary student, for whose guidance the work is intended. It is obvious from the plan followed that the author believes, with Woehler, that "it is easier for most heads to reach a clear comprehension of general relations and rules through the consideration of a specific case, than to accommodate themselves to the application of general rules and principles to special cases." To those who concur in this opinion the book will recommend itself as one of more than ordinary merit.

H. N. MORSE.

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## NOTES.

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*Note to Paper on Nitrogen Iodide in April Number of this Journal.*

It is interesting to compare the formula suggested for nitrogen iodide and the various substitution products from it containing hydrogen with that given by Zorn (*Ber. d. chem. Gesell.* 11, 1630) for the compound he obtains by the action of ethyl iodide upon nitrosyl silver, which he views as diazoethoxane, and describes as "almost as explosive as nitrogen chloride." Griess (*Ber. d. chem. Gesell.* 10, 528) has proposed to consider other diazo-compounds as containing pentad nitrogen.

J. W. MALLET.

### *Malleable Nickel and Cobalt.*

TH. FLEITMANN has succeeded in obtaining the metals nickel and cobalt in malleable condition by fusing them with a very small quantity of metallic magnesium. He suspected that the absorption of carbon monoxide by the metals might be the cause of their want of malleability, and introduced the magnesium for the purpose of destroying the gas, as this metal is known to decompose the oxides of carbon. The success was very surprising. An addition of  $\frac{1}{2}$  per cent. of metallic magnesium changes the structure of the metals entirely. They

can now be easily welded when hot. Nickel is malleable even when cold, while cobalt becomes extremely hard when cold, so that it will probably be applicable for cutting instruments.

At the same time the cast metals are very compact, and are almost as solid and tough as cast steel, so that the metallic parts of harness and similar objects may be made from them.

Both metals take a very high polish, and resist the action of the atmosphere very well. The author has also succeeded in welding malleable nickel and cobalt together with steel and iron, so that the pieces of iron and steel that are coated on one or both sides with nickel or cobalt may be beaten out to the thinnest plates without any separation of the metals.

Magnesium also causes a remarkable change of structure in other metals. A coarse-grained steel becomes fine-grained on the addition of one-fifth per cent. of magnesium. In performing the experiments referred to, the magnesium must be introduced through a hole in the cover of the crucible after the oxygen has been first removed by the addition of a few pieces of charcoal. Without this precaution violent explosions are apt to occur.—(*Ber. d. chem. Gesell.* 12, 454.)

#### *Stop-Cock of easy Construction.*

In the *Zeitschrift f. analytische Chemie*, 18, 258, is described a simple form of stop-cock, made of glass tubes and corks, devised by Lecoq de Boisbandran. A much simpler form may be constructed as follows:

Take two glass tubes, one of which slides easily into the other, close the end of the smaller tube in the flame of a Bunsen's burner, and make an opening about an inch from the closed end by filing crosswise with a rat-tail file. Connect the two tubes by a piece of rubber tubing, which should fit the smaller tube closely, and the stop-cock is complete. When the smaller tube is pushed into the larger one the cock is open, when shoved back into the rubber tube the opening in the small tube is covered by the rubber wall and the passage of liquids or gases prevented. The accompanying figures make this clear. Fig. 1 represents the cock open. Fig. 2 shows the cock closed.



Fig. 1.

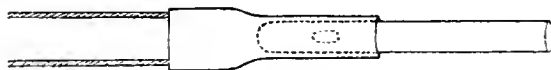


Fig. 2.

EDWARD HART.

*Treatment of Bunsen's Elements.*

In order to keep the metallic connections of galvanic batteries bright, and thus keep the batteries in good running order. BEILSTEIN and JAWEIN recommend the use of *oleonaphtha* as a lubricant. This material is obtained in large quantities from Caucasian petroleum and is sold at a moderate price.\* The connections remain unchanged for a long time. Not the least formation of rust was noticed on the binding screws which were on the charcoals placed in nitric acid.—(*Ber. d. chem. Gesell.* 12, 448.)

*Analysis of a Calculus found in a Deer.*

This rather interesting specimen was given me by Mr. Hall, student in the Medical Department of the University. It was found by him in the pelvis of the kidney of a doe, which had been shot by a party hunting in the northwestern portion of this State.

As the investigation of such calculi very frequently affords some interesting results, I subjected this specimen to both a qualitative and quantitative examination.

The size of the calculus was equal to that of the egg of a pigeon. It possessed a fawn color, and consisted of three layers encircling a rather large nucleus, which presented a granular sandstone-like appearance. The layers were exceedingly thin, and seemed to have grown out from carbonaceous deposits, which were detected in various portions of the calculus.

Upon testing the nucleus qualitatively the presence of silica, ferric oxide, calcium oxide and phosphoric acid was clearly shown. The surrounding layers were found to contain calcium and magnesium oxides, phosphoric acid, sodium, potassium, uric acid and another organic compound. The latter was extracted from the finely divided material by boiling the same for some time with alcohol. The alcoholic filtrate yielded upon evaporation a gelatinous mass, which proved to be the sodium salt of an acid, which formed strong, colorless needles, exhibiting an hexagonal structure. Upon gently warming this crystalline mass with a grain or two of sugar and a drop of concentrated sulphuric acid, a beautiful purple color appeared. It is true, several acids occurring in the bile give the same reaction with sugar and sulphuric acid, but not any of them, so far as I know, possess the crystalline form of the above compound, nor yield a sodium salt similar to that mentioned above. The only acid which in the least corresponds to the previous description is that known as *lithofellic acid*, which was discovered a number of years ago† in a va-

\*Probably the lubricating oil obtained from petroleum in this country would answer the purpose equally well.—Ed.

†*Ann. der Chemie*, 39, p. 237, 242; 41, p. 150.

riety of the deer family. The want of sufficient material prevented me from making other and more decisive tests to discover the real character of this compound.

As the layers surrounding the nucleus were alike in chemical composition they were finely divided, and a quantitative analysis made of the mixture. Analysis:

43.15	per cent.	P <sub>2</sub> O <sub>5</sub> .
.91	"	MgO.
2.60	"	Loss on ignition.
2.50	"	CaO.
51.00	"	alkaline oxides.
<hr/>		
100.16		

EDGAR F. SMITH.

*Note on the Absorption Spectrum of Uranine.*

Having only a small quantity of uranine, I took for the experiment .0038 gram. I dissolved this quantity in 500 cc. of water and examined in a glass cell 12 mm. in diameter. .0038 g. in 500 cc. gave almost black band, the extreme edge of which is almost coincident with the F line of the solar spectrum. The absorption band extended from this point almost half way through the green. .0038 g. in 1000 cc. gave a distinct band. .0038 g. in 2000 cc. gave still a distinct band. .0038 g. in 4000 cc. gave a faint yet readily detected band. .0038 g. in 8000 cc. gave no distinct absorption.

From the above it is seen that one part of uranine in one million parts of water is readily detected by its deportment in the spectrum. By increasing the thickness of the liquid traversed the delicacy of the reaction could be made more striking. I employed indirect sunlight for producing the spectrum, and Vogel's spectroscope in the observations. The examinations were made immediately after the solution of the substance.

H. W. WILEY.

*Note on the Delicacy of the Test for Cobalt with Cyanide of Potassium and yellow Sulphide of Ammonium.\**

Mr. G. L. SPENCER has made some experiments to determine the limit of the above-mentioned reaction for cobalt. .0924 g. cobaltous nitrate was dissolved in 100 cc. of water. 1 cc. of the solution in 1 cc. of water on addition of the reagents gave a pronounced red color. .2 cc. in 1 cc. of water gave still a distinct red color. .15 cc gave in 1 cc. water a faint red color. .1 cc. in 1 cc. water did not give an appreciable red tint.

Thus it is seen that less than one-tenth of a milligram of cobaltous nitrate in 1 cc. of water can be easily detected by

\* Tattersall, Chem. News, Feb. 14, 1879.

the above method. This quantity evaporated to dryness and collected as fully as possible failed to give a blue color with a borax bead. Sulphide of ammonium and cyanide of potassium are therefore more delicate reagents for cobalt than borax. The presence of zinc, nickel and manganese salts diminishes slightly the delicacy of the reaction. One milligram of the cobalt salt, however, in 1 cc. water was still to be detected in the presence of three hundred times that weight of the compounds of the other three substances. I am having my students use this method and with satisfactory results.

H. W. WILEY.

*New Compounds of Ammonia with Hydrochloric Acid.*

In studying the vapor densities of ammonium compounds L. TROOST has been led to the discovery of a number of curious compounds of ammonia with hydrochloric and other acids both inorganic and organic. Two new compounds of ammonia and hydrochloric acid are described. To obtain them, ammonia gas, pure and perfectly dry, is saturated with pure hydrochloric acid gas. The ammonium chloride thus formed is distilled in a closed vessel in the presence of a large excess of ammonia gas, and the products cooled at varying temperatures. Two definite crystalline substances were obtained. The first has the formula  $\text{HCl}, 4\text{NH}_3$ , and is called by Troost tetra-ammonia chlorhydrate. It is anhydrous and melts at  $+7^\circ$ . Its crystals strongly depolarize light and consequently do not belong to the same system as those of ordinary ammonium chlorhydrate. If the tension of ammonia given off by this substance be measured, it is found to remain constant for a given temperature, while the volume of gas existing at the surface of the dissociating substance is varied; just as the tension of water vapor in presence of liquid water remains constant for a given temperature with varying volume. This characteristic the author considers sufficient of itself to prove the definite existence of the substance described. Its tension of dissociation ranges from 140 mm. at  $-36^\circ$  to 1800 mm. at  $+8^\circ$ .

The second substance obtained has the formula  $\text{HCl}, 7\text{NH}_3$ . It melts at  $-18^\circ$ , but may be cooled to  $-40^\circ$  before solidification. The author was unable to distinguish its crystalline or optical properties from those of the preceding substance, but its appearance was quite different. The characteristics of its dissociation were the same as in the case of tetra-ammonia chlorhydrate, into which it is transformed by loss of ammonia. Its tension of dissociation ranges from 580 mm. at  $-36^\circ$  to 1130 mm. at  $-21^\circ$ . The author thinks that this is not the last term of this singular series. He was arrested at this point only by the difficulty of maintaining lower temperatures

constant. Analogous compounds with other acids are to be described in a future communication.—(*Compt. rend.* 88, 579, March 17th, 1879.)

*Vapor Density of some Inorganic Bodies.*

VICTOR MEYER and CARL MEYER have begun to apply the method recently described by them for the determination of vapor densities, to the study of some difficultly volatile inorganic bodies. Phosphorus pentasulphide, fusing at  $274^{\circ}$ – $276^{\circ}$ , and boiling, according to Hittorf, at  $530^{\circ}$ , was converted into vapor in an atmosphere of nitrogen. The results obtained correspond to the vapor density 7.63 and 7.67, while the formula  $P_2S_5$  requires 7.67. Hence it is seen that the pentasulphide *does not suffer dissociation* when converted into vapor, but that its vapor consists of molecules of the composition  $P_2S_5$ .

Since Bunsen determined the specific heat of indium this metal has been classed with aluminium and not with zinc as previously. No compound of indium had ever been converted into the form of vapor, and hence it was not known whether the chloride is analogous to those of iron and aluminium, *i. e.*  $In_2Cl_6$ ; or has the simpler formula  $InCl_3$ , or, in other words, whether indium is quadrivalent or trivalent. The authors have now determined the specific gravity of the vapor of indium chloride and obtained the number 7.87. The formula  $InCl_3$  requires 7.60, and  $In_2Cl_6$  requires 15.20, so that it is plain that analogy does not exist between this chloride and those of iron and aluminium; and indium is seen to be trivalent. The conversion of the chloride into vapor was effected at red heat.—(*Ber. d. chem. Gesell.* 12, 609.)

*Purification of Mercury.*

In the last number of this Journal, page 68, a method recommended by Bruehl for the purification of mercury is briefly described. LOTIAR MEYER now describes another method for which he claims certain advantages over the method of Bruehl. It consists in allowing the impure mercury to fall through a solution of ferric chloride. The solution is placed in a glass tube from a meter to a meter and a half long and three cm. wide. The lower end of the tube is placed in a cylinder which has a side opening at the top. As the mercury passes through the solution it breaks up into very fine drops, which do not flow together because they are covered with a very thin coating of chloride or subchloride. The following portions of mercury, however, press them together. The mercury purified by this method is pure enough for use in capillary experiments.—(*Ber. d. chem. Gesell.* 12, 437.)

*On the Preparation of Barium from Barium-amalgam.*

Some years ago Crookes described a method for the preparation of metallic barium from the amalgam. The amalgam is readily prepared by adding sodium-amalgam to a saturated, aqueous solution of barium chloride. When the amalgam is distilled, mercury passes off, and a substance is left behind which Crookes described as the metal barium. DONATH has repeated the experiments of Crookes, and finds that the product obtained is by no means barium, but rather an amalgam containing a considerable amount of barium. In different specimens there were found 62–77 per cent. of mercury. It is not possible to obtain a purer preparation even in a porcelain tube heated nearly to white heat. Now and then small pellets of a bronze-colored metal were obtained, but this color did not appear in the interior of the pieces. Nevertheless the color of pure barium is yellow, as Bunsen and Matthiessen state in describing the metal prepared by the electrolysis of the fused chloride.—(*Ber. d. chem. Gesell.* 12, 745.)

*On the Relations of Cantharidin Derivatives to the Ortho-series.*

J. PICCARD has found that when the commercial article, cantharidin, is heated with phosphorus pentasulphide, a very good yield of orthoxylene is obtained. The hydrocarbon yields by oxidation with nitric acid, first, orthotoluic acid, and, by further treatment, phthalic acid. This method is by far the most convenient for the preparation of small quantities of pure orthoxylene. The relation between cantharidin and orthoxylene is similar to that which exists between camphor and cymene (paraethylmethylbenzene), the former being readily transformed into the latter by treatment with phosphorus pentasulphide.—(*Ber. d. chem. Gesell.* 12, 577.)

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# AMERICAN CHEMICAL JOURNAL.

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## RESEARCHES ON THE COMPLEX INORGANIC ACIDS.\*

BY WOLCOTT GIBBS, M. D.

*Rumford Professor in Harvard University.*

I propose the term "complex inorganic acid" for a class of compounds which may be considered as formed by the union of two or more acids with elimination of water in such a manner as to form a whole which in its chemical relations behaves like an acid containing a single radical. Compounds of this character were observed at an early period in the history of chemistry, but their real nature was for a long time entirely unknown, and our positive knowledge of the subject dates from the discovery of the silico-tungstates by Marignac in 1861.† Berzelius had long before described and analyzed a compound which we should now write



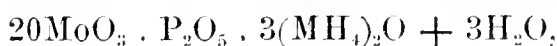
the chemical relations of which are still to be studied.‡ He had also noticed the formation of peculiar yellow compounds when phosphoric or arsenic acids are digested with molybdic

\* Presented to the American Academy of Arts and Sciences, June 24th, 1879. Communicated by the author.

† Ann. de Chimie et de Physique, (4.) 3, 55.

‡ Lehrbuch der Chemie, 3, 1058.

teroxide.\* These were again noticed and partially studied by Svanberg and Struve,† who employed a solution of ammoniac molybdate as a test for the presence of phosphoric acid. Sonnenschein‡ appears to have first shown that phosphoric oxide was an essential constituent of the yellow compound formed. Finally Debray assigned to the ammonium salt the formula

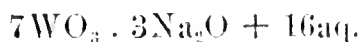


and separated the corresponding acid.

In a paper presented to the Association of German Naturalists and Physicians in August, 1872,§ Scheibler described salts of two different phosphotungstic acids, and gave formulas for the acids themselves, as well as for a sodium salt belonging to a third series, all of which, however, he regarded as provisional. Since then nothing further has appeared upon the subject from Scheibler's pen, and I have consequently felt at liberty to include the phosphotungstates in my own work.

My investigation of the complex inorganic acids had advanced but little before I found it necessary to study the alkaline salts of tungstic acid with special care. This study has alone occupied a great deal of time, and has proved one of extraordinary difficulty, in spite of the previous labors of Laurent, Lotz, Scheibler, Zettnow, Marignac, and others. The difficulties in question are mainly these:—

1. The alkaline tungstates are numerous and unusually complex. Salts of essentially different formulas approach so closely in percentage composition, that the differences lie very near the unavoidable errors of analysis. Thus Scheibler maintains that the formula of a particular sodium salt is



while, according to Marignac, the same salt must be represented by



The analyses are hardly sufficiently close to decide the question upon purely analytical grounds.

\* Lehrbuch, 3, 1044

† K. Sv. Vet. Handlingar, 1848, p. 1.

‡ Journal für prakt. Chemie, 53, 342.

§ Berichte der deutschen chem. Gesell, 5, 801.

2. Almost all the alkaline tungstates are efflorescent in a very marked degree.

3. The salts of one series agree so closely in chemical properties with those of the next, that distinctive tests are wanting, and analysis does not always suffice to distinguish two salts even when unmixed. Mixtures are naturally very hard to deal with.

4. Monoclinic and triclinic forms predominate very largely, but owing to rapid efflorescence it is very difficult to make good measurements of crystals. The resemblance between the forms of different compounds is frequently very close.

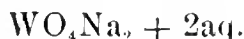
5. Many salts are decomposed by boiling, or even by hot water, yielding two or more different salts in solution. These usually recombine in the act of crystallization or on cooling the solution, but the reactions of hot and cold solutions are often, as I shall show, very different.

In determining the tungstic oxide in these compounds, I have employed the method of Berzelius with mercurous nitrate almost exclusively, but I have modified the process slightly so as to gain materially in accuracy. To the hot solution of the tungstate mercurous nitrate is added until in small excess. Mercuric oxide, prepared by precipitating the chloride by sodic hydrate, is then added until the yellow mercurous tungstate takes a reddish hue which is persistent after boiling. If the solution is boiled before filtering it clears rapidly, and the precipitate becomes rather more compact. The filtration and washing are then very easy and expeditious. The precipitate must be ignited as long as it loses weight. By this process Dr. Gooch, my assistant, obtained results which in two successive analyses of the same preparation rarely differed by 0.1 p. ct. The water determinations were always made by simple ignition. They almost invariably agree within a few hundredths. In the greater number of cases the alkaline base was determined from the loss, as the results obtained in this manner are far more accurate than those yielded by the direct method. But in some doubtful salts the alkali was determined directly. Ammonia was always estimated by boiling the compound with an excess of sodic hydrate, collecting the ammonia in chlorhydric acid, and weighing it as chloride.

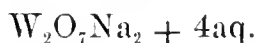
The only objection to the method of determining tungstic oxide above given is, that the precipitate of mercurous tungstate is rather voluminous, so that it is necessary to work with quantities of alkaline tungstate not much exceeding one gram in weight. I endeavored to overcome this difficulty by omitting the mercuric oxide and evaporating the solution and precipitate, after the addition of mercurous nitrate, to perfect dryness in a water bath, continuing the heat until all the free nitric acid was expelled. This method gave results which corresponded very closely with those obtained by the use of mercuric oxide to neutralize the free nitric acid, and in consequence of the extremely compact form of the dry mercurous tungstate, permitted the employment of much larger quantities of salt for analysis. On the other hand, it presents another difficulty, arising from the fact that the dry mercurous tungstate adheres with excessive tenacity to the evaporating vessels, whether of glass, porcelain, or platinum, so that the first method is on the whole to be preferred.

The separation of tungstic oxide from other bases is best effected by fusing the salt with an excess of potassio-sodic carbonate and dissolving out the alkaline tungstates formed.

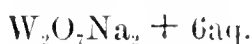
Normal sodic tungstate has long been known, and all the analyses concur in assigning to it the formula



It is now to be had from various German firms in a state of purity, and forms the most convenient material for the study of the compounds of tungsten. The acid salt analyzed by Anthon, and to which the formula



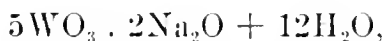
was long ascribed, is now well known to have an entirely different composition; but Lefort\* has recently endeavored to show that ditungstates and tritungstates really exist, and has described a number of salts of each series. Lefort obtains sodic ditungstate by adding glacial acetic acid to a saturated solution of the neutral salt until the reaction with litmus becomes acid. After a day or two the salt separates in long prismatic crystals, with the formula



\* Ann. de Chimie et de Physique, (5.) 9, 35.

I have repeatedly attempted to prepare the ditungstate by this process, but without success in any one instance, the resulting salts being, as I shall show further on, in all cases very different in composition. Lefort prepared sodic tritungstate by pouring a concentrated solution of the ditungstate into a boiling solution of glacial acetic acid. His analyses agree fairly well with his formulas, and I have adopted his results without question, in the belief that my own inability to reproduce them was due to the omission in his paper of some matter of detail which appeared insignificant, but which was really important.

*Ten to Four Sodium Salt.*—The salt to which I have given this name appears to have been first observed by Forcher,\* who obtained it by passing a current of carbonic dioxide for some days through a solution of the normal tungstate. Forcher gives the formula



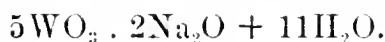
and suggests, though without adducing any evidence in support of his view, that it may be a double salt, with the formula



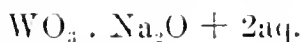
Marignac, who appears to have been unacquainted with Forcher's paper, soon afterward described the same salt as an accidental product, attributing to it the formula



Finally, Lefort† obtained it by the action of acetic acid upon a solution of the normal tungstate, and, without citing the results of Forcher, also proposed the formula



I have obtained the salt by the following process, which appears to be the most convenient. Normal sodic tungstate,

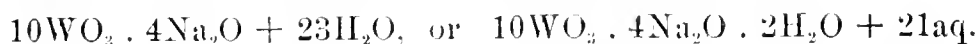


is to be dissolved in water, and acetic acid added, in small portions at a time, to the boiling solution, until the reaction becomes strongly acid. Alcohol then precipitates the 10:4 tungstate as a heavy oil, which soon becomes a solid mass.

\* Wiener Akad. Berichte, H. 2, 155.

† Loc. cit.

The solution on standing some days deposits colorless crystals, which are usually much twinned, and, according to Marignac, belong to the monoclinic system. They effloresce readily in dry air and are soluble, according to Forcher's determination, in 12.6 parts of water at 22° C. When heated they fuse to a yellow liquid, which on cooling gives a white crystalline mass nearly insoluble in cold water but dissolved by long boiling. I assign to the crystallized hydrate the formula



with which all the analyses agree very closely. Of the salt,

I.	{	1.4152 gr. lost on ignition	= 13.88 p. et.
	{	0.4095 gr. gave 0.3194 gr. $\text{WO}_3$	= 77.99 "
II.	{	1.1182 gr. lost on ignition	0.1558 gr. water = 13.94 "
	{	0.8950 gr. gave 0.6968 gr. $\text{WO}_3$	= 77.85 "
III.	{	1.3594 gr. lost on ignition	0.1862 gr. water = 13.70 "
	{	0.5340 gr. gave 0.4155 gr. $\text{WO}_3$	= 77.80 "
IV.	{	1.1660 gr. lost on ignition	0.1624 gr. water = 13.93 "
	{	0.5981 gr. gave 0.4659 gr. $\text{WO}_3$	= 77.89 "
V.	{	1.3594 gr. lost on ignition	0.1862 gr. water = 13.70 "
	{	0.5340 gr. gave 0.4155 gr. $\text{WO}_3$	= 77.80 "

The formula  $10\text{WO}_3 \cdot 4\text{Na}_2\text{O} + 23\text{aq.}$  requires

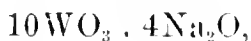
	Calc'd.	1.	2.	3.	4.	5.	Forcher.	Marignac.	
10WO <sub>3</sub>	2320	77.80	77.99	77.85	77.80	77.89	77.80	77.82	77.88
4Na <sub>2</sub> O	248	8.32	8.13	8.21	8.50	8.18	8.50	8.16	8.39
23H <sub>2</sub> O	414	13.88	13.88	13.94	13.70	13.93	13.70	13.88	13.53
	<hr/>	<hr/>					<hr/>	<hr/>	
	2982	100.00					99.86	99.80	

The means of all these analyses may be compared with the three formulas above given.

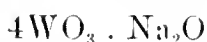
			WO <sub>3</sub>	Na <sub>2</sub> O	H <sub>2</sub> O		
For the ratio	10	4	22	78.27	8.37	15.36	
“	“	10	4	24	77.63	8.16	14.21
“	“	10	4	23	77.80	8.32	13.88
Means of new analyses,				77.86	8.30	13.83	

The analyses therefore leave no reasonable doubt as to the true constitution of the salt. The solution of the 10 : 4 sodic

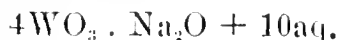
tungstate has a distinct acid reaction, but it is very difficult to determine the limits of the basicity in this series, because no salts could be obtained having a number of molecules of fixed base higher than four. On the other hand, the white insoluble mass obtained by igniting the crystalline hydrate must have the formula



and I consider it a true pyro-salt. When boiled for some time with water, the pyro-salt dissolves and the original salt crystallizes from the solution. The case appears to be exactly analogous to that of sodic metatungstate, the insoluble



of Scheibler and Marignac, giving the normal sodic metatungstate,



when heated with water in a sealed tube. The reactions of the 10 : 4 salt with metallic solutions are extremely similar to those of the 12 : 5 salt.



so that in fact it is difficult to distinguish between the two in any other way than by the habitus of the crystals and by analysis.

When the 10 : 4 salt is dissolved in water and a current of sulphydric acid gas passed into the solution to the point of saturation, the liquid becomes at first yellow, and finally orange red. On standing or evaporation, it deposits brown tungstic sulphide,  $\text{WS}_3$ , and the still faintly yellow mother liquor gives fine colorless triclinic crystals, which are separate and distinct, not twinned or aggregated in masses like the 10 : 4 salt. These crystals after recrystallization have the formula of the 12 : 5 salt presently to be described, namely,

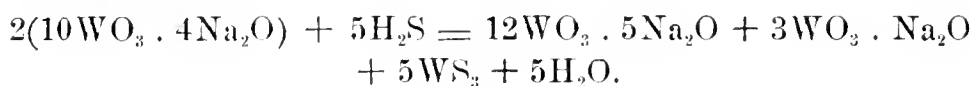


as the following analyses show :—

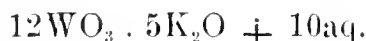
1.6491 gr. gave	1.2760 gr. $\text{WO}_3$	= 77.38 p. ct.
2.3696 gr. lost	0.3308 gr. water	= 13.96 “
2.0037 gr. “	0.2790 gr. “	= 13.92 “

		Calc'd.	Found.
12WO <sub>3</sub>	2784	77.38	77.38
5Na <sub>2</sub> O	330	8.61	8.68
28H <sub>2</sub> O	504	14.01	13.92 13.96
	<hr/> 3618	<hr/> 100.00	

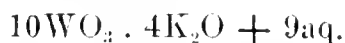
The formation of the 12:5 from the 10:4 salt is easily explained, as well as the separation of the tungstic sulphide, since we have



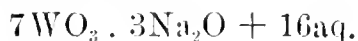
A concentrated solution of the 10:4 sodium salt is resolved by boiling into the 12:5 salt and other compounds difficult to isolate in a state of purity. When a hot solution of potassic bromide or nitrate is added to a boiling solution of the 10:4 sodium salt, a white crystalline precipitate is speedily formed, which has the formula



But if a cold solution of a potassic salt is added to a cold solution of the 10:4 sodium salt, a white crystalline precipitate is formed, which has the formula



*Twelve to Five Sodium Salt.*—This is the salt to which Scheibler gives the formula



and which Marignac writes

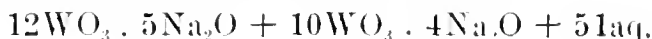


According to Lotz, the salt contains fourteen atoms of water in place of sixteen as found by Scheibler. I have adopted the formula of Marignac, which agrees best with the analyses. In preparing this salt I have employed Scheibler's method, which consists in nearly neutralizing a boiling solution of the neutral tungstate,  $\text{WO}_4\text{Na}_2 + 2\text{aq.}$  by chlorhydric acid. When the proper quantity of chlorhydric acid is added, the 12:5 salt is formed at once, and crystallizes from the solution in large colorless crystals, which, according to Scheibler, are

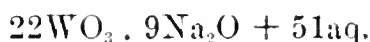
monoclinic; according to Marignac, triclinic. If the proportion of chlorhydric acid is just sufficient to give an onion-red reaction with litmus, crystals are obtained, which are either a combination or a mixture of equal molecules of the 10:4 and 12:5 salts. These crystals are, according to Dr. Gooch, triclinic; their habitus resembles that of the 12:5 rather than that of the 10:4 salt. In this salt, in two different preparations carefully dried and pressed with woollen paper,

I.	{	1.2546 gr. gave	0.9725 gr. $\text{WO}_3$	= 77.51 p. et.
		1.2320 gr. "	0.9554 gr. "	= 77.55 "
		1.4680 gr. lost	0.2035 gr. water	= 13.86 "
		1.7511 gr. "	0.2431 gr. "	= 13.88 "
II.	{	1.0842 gr. gave	0.8407 gr. $\text{WO}_3$	= 77.54 "
		1.0908 gr. "	0.8450 gr. "	= 77.47 "
		1.6919 gr. lost	0.2362 gr. water	= 13.96 "
		1.5259 gr. "	0.2125 gr. "	= 13.93 "

The analyses agree closely with the formula



or,



which requires

		Calc'd.	Mean.	Found.			
22 $\text{WO}_3$	5104	77.57	77.52	77.51	77.55	77.54	77.47
9 $\text{Na}_2\text{O}$	558	8.48	8.57	...	...	...	...
51 $\text{H}_2\text{O}$	918	13.95	13.91	13.86	13.88	13.96	13.93
	<u>6580</u>	<u>100.00</u>	<u>100.00</u>				

I have already stated that in repeated trials I had not been able to obtain sodic ditungstate described and analyzed by Lefort, though the process given by him was followed implicitly. In one experiment the crystals obtained gave on analysis results which correspond closely with the formula



1.9868 gr. lost on ignition	0.2786 gr. water	= 14.02 per et.
1.2870 gr. "	0.1806 gr. "	= 14.01 "
0.9365 gr. gave	0.7243 gr. $\text{WO}_3$	= 77.34 "
1.3560 gr. "	1.0483 gr. "	= 77.31 "

	Calc'd.	Found.	
12WO <sub>3</sub>	77.38	77.34	77.31
5Na <sub>2</sub> O	8.61	8.66	
28H <sub>2</sub> O	14.01	14.02	14.01
	<hr/> 100.00		

In this experiment the normal tungstate was dissolved in cold water to a very strong solution, glacial acetic acid was added in excess, and the whole allowed to stand for twenty-four hours, when prismatic crystals separated. In a second experiment a concentrated solution of sodic tungstate was heated to the boiling point and ordinary acetic acid added in excess. Alcohol then threw down a pasty mass, which, after re-resolution in water and crystallization, gave on analysis results which corresponded with the formula



1.0861 gr. lost on ignition	0.1492 gr. water	= 13.74 p. et.
1.3830 gr. " "	0.1895 gr. " "	= 13.70 "
0.8884 gr. gave	0.6899 gr. WO <sub>3</sub>	= 77.66 "
1.2746 gr. " "	0.9902 gr. " "	= 77.69 "

	Calc'd.	Found.	
22WO <sub>3</sub>	77.57	77.67	77.69
9Na <sub>2</sub> O	8.48	8.60	
51H <sub>2</sub> O	13.95	13.70	13.74
	<hr/> 100.00		

The small differences between the calculated formula and the direct results of the analyses, in this instance, are exactly such as would be produced by the admixture of a small percentage of the 10 : 4 sodium salt, which, as I have shown above, is formed when a solution of neutral sodic tungstate is boiled for some time with an excess of acetic acid. The general result of my own study of the action of acetic acid upon the neutral tungstate is, that we obtain the 12 : 5, the 22 : 9, or the 10 : 4 salt, according to the circumstances of the case, the constitution of the salt formed depending mainly upon the degree of concentration of the acid and upon the duration of its action. These results are in no way inconsistent with those of Lefort, and his analyses seem to leave no

reasonable doubt that he obtained various salts to be classed as ditungstates and tritungstates.

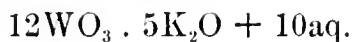
*Potassic Tungstates*.—When a hot solution of the 10 : 4 sodium salt is mixed with a hot solution of potassic nitrate, a white precipitate shortly appears in small colorless crystalline scales, which may be recrystallized by projecting them in very small quantities at a time into boiling water. This method, which was first given by Scheibler, enables us to redissolve the salt in water without loss from the excessively violent succussions which occur on heating the salt with water in the usual manner. The salt requires a rather large quantity of water for solution, and crystallizes almost completely from the cold liquid. Of this salt in the first preparation,—

0.9888 gr. lost on ignition	0.0510 gr. water =	5.18 p. ct.
0.6513 gr. “ “	0.0358 gr. “ =	5.49 “
1.1663 gr. “ “	0.0610 gr. “ =	5.23 “
1.1287 gr. “ “	0.0596 gr. “ =	5.28 “
1.0068 gr. gave	0.8173 gr. $\text{WO}_3$ =	81.21 “

In a second preparation,—

1.4312 gr. lost on ignition	0.0751 gr. water =	5.25 p. ct.
1.5846 gr. “ “	0.0832 gr. “ =	5.25 “
0.5786 gr. gave	0.4686 gr. $\text{WO}_3$ =	80.99 “
0.4773 gr. “	0.3875 gr. “ =	81.20 “
1.8957 gr. “	1.5370 gr. “ =	81.08 “

These analyses lead to the formula



which requires:—

		Calc'd.	Mean.	1.	Found.		
					2.	3.	
$12\text{WO}_3$	2784	81.02	81.12	81.21	80.99	81.20	81.08
$5\text{K}_2\text{O}$	472	13.73	13.62	...	...	...	...
$10\text{H}_2\text{O}$	180	5.25	5.26	5.29*	5.25	5.25	...
		<hr/>	<hr/>				
		3436	100.00				

Marignac gives eleven molecules of water. Scheibler gives the formula  $7\text{WO}_3 \cdot 3\text{K}_2\text{O} + 6\text{aq.}$ , but his analyses agree better with that of Marignac.

\* Mean of the four determinations of water in the first preparation.

When normal potassic tungstate,  $\text{WO}_4\text{K}_2$ , is evaporated to dryness with boric hydrate, and the soluble salts are washed out from the mass, a salt is obtained which after recrystallization has the formula



The same salt is formed when cold solutions of potassic nitrate or bromide are added to cold solutions of the 10 : 4 sodium salts. It resembles the 12 : 5 potassium salt, already described, so closely that it is difficult to distinguish between the two. This salt has not been described by other writers upon the subject. In preparation *a*, from the action of boric acid upon normal potassic tungstate,

0.4566 gr. gave                      0.3714 gr.  $\text{WO}_3$  = 81.34 p. ct.  
0.5915 gr. lost on ignition   0.0331 gr. water = 5.59 "

In preparation *b*, from the action of acetic acid upon the normal potassium salt,

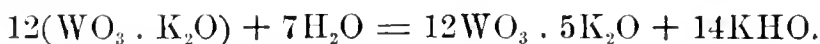
0.7418 gr. gave                      0.6024 gr.  $\text{WO}_3$  = 81.21 p. ct.  
1.1104 gr. lost on ignition   0.0610 gr. water = 5.49 "  
0.7060 gr. gave                      0.5736 gr.  $\text{WO}_3$  = 81.27 "  
1.0266 gr. lost on ignition   0.0556 gr. water = 5.42 "

These analyses correspond best with the formula



		Calc'd.	Mean.			
10 $\text{WO}_3$	2320	81.13	81.27	81.34	81.2	81.27
4 $\text{K}_2\text{O}$	377.6	13.20	13.23	13.07	13.30	13.31
9 $\text{H}_2\text{O}$	162	5.67	5.50	5.59	5.49	5.42
	<hr/> 2859.6	<hr/> 100.00				

It is probable that the salt had lost a little water by efflorescence. When normal potassic tungstate is dissolved in boiling water, it is decomposed into free alkali and 12 : 5 acid tungstate. The decomposition may be represented by the equation,



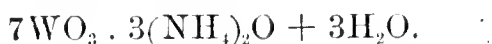
In the acid salt formed in this manner,

0.7738 gr. lost on ignition   0.0414 gr. water = 5.35 p. ct.  
1.0385 gr. gave                      0.8411 gr.  $\text{WO}_3$  = 80.99 "



		Calc'd.	Mean.	Found.	
12WO <sub>3</sub>	2784	88.32	88.32	88.34	88.31
5(NH <sub>4</sub> ) <sub>2</sub> O	260	8.24	8.03	8.15	7.92
6H <sub>2</sub> O	108	3.44	3.64	3.51	3.77
	<hr/> 3152	<hr/> 100.00	<hr/> 99.99		

Marignac found in this salt five molecules of water. Lotz and Scheibler gave it the formula



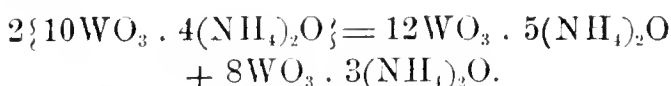
Marignac has also described and analyzed an ammonium salt to which he gives the formula



I should double this formula, and write it



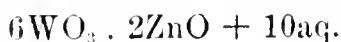
so that it would then belong to the series of 10 : 4 salts, the existence of which I have endeavored to establish. According to Marignac, it breaks up by solution in water into the 12 : 5 and 8 : 3 salts.



*Zinc Salts.*—When a solution of zineous sulphate is added in small excess to a hot solution of the 10 : 4 sodic tungstate, no precipitate is produced at first, but after a few seconds beautiful aggregates of white needles make their appearance, and continue to be deposited for some time. They are almost perfectly insoluble in boiling water. For analysis they were washed with cold water and dried in pleno over sulphuric acid. The zinc salt is soluble both in an excess of zineous sulphate and of sodic tungstate; hence the precipitate which is at first formed is instantly redissolved and does not become permanent until a small excess of the sulphate is added. In this salt,

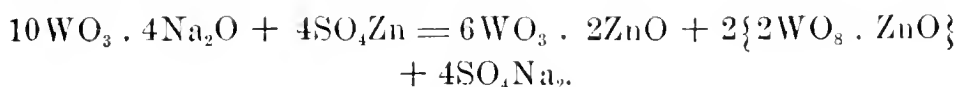
0.3342 gr. lost on ignition	0.0349 gr. water = 10.44 p. ct.
0.6392 gr. gave	0.5128 gr. WO <sub>3</sub> = 80.50 “
1.0205 gr. “	0.8200 gr. “ = 80.35 “

These analyses correspond with the formula



		Calc'd.	Found.
6WO <sub>3</sub>	1392	80.27	80.50      80.35
2ZnO	162	9.34	9.14 (loss)
10H <sub>2</sub> O	180	10.39	10.44
	<hr/>	<hr/>	
	1734	100.00	

From this it appears that the zinc salt is formed by the decomposition of the 10 : 4 sodic tungstate. The result may be expressed by the equation,

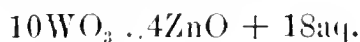


The zincous ditungstate, as Lefort has shown, is readily soluble in water and remains in solution.

When a cold solution of zincous sulphate is added to a cold solution of the 10 : 4 sodium salt, a different result is obtained. A white precipitate is at first formed as before, which instantly redissolves. After a small excess of the sulphate has been added, the solution gives in a short time colorless needles of a second zinc salt. Like the 6 : 2 salt first described, this is insoluble in water, cold or hot, but readily dissolves in an excess of the tungstate or sulphate. When a large excess of the sulphate is present, the zincous tungstate does not separate from the solution. Of this salt in one preparation, dried over SO<sub>4</sub>H<sub>2</sub>:

0.6586 gr. lost on ignition	0.0706 gr. water	= 10.72 p. et.
	{ 0.0638 gr. ZnO	= 10.82    "
0.5894 gr. gave	{ 0.4606 gr. WO <sub>3</sub>	= 78.16    "

These analyses lead to the formula

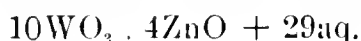


which requires

		Calc'd.	Found.
10WO <sub>3</sub>	2320	78.16	78.16
4ZnO	324	10.92	10.82
18H <sub>2</sub> O	324	10.92	10.72
	<hr/>	<hr/>	<hr/>
	2968	100.00	99.70

In a second preparation of the same salt, dried by woollen paper, 1.0006 gr. gave by ignition 0.1663 gr. water, also 0.7322 gr. WO<sub>3</sub> and 0.1048 gr. ZnO = 16.62 p. et. water, 73.18 p. et. WO<sub>3</sub>, and 10.47 p. et. ZnO.

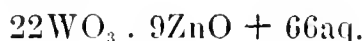
These results correspond to the formula



which requires

		Calc'd.	Found.
10WO <sub>3</sub>	2320	73.27	73.18
4ZnO	324	10.24	10.47
29H <sub>2</sub> O	522	16.49	16.62
	<hr/> 3166	<hr/> 100.00	<hr/> 100.27

When a cold solution of zineous sulphate is added to a cold solution of the 22-atom sodium salt a precipitate is formed, which redissolves precisely as in the last-mentioned cases. After the solution of zinc has been added in small excess, white needles separate, which are insoluble in water, and have the formula



as the following analyses show :

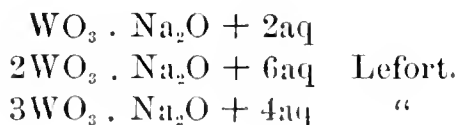
1.4620 gr. gave 0.2509 gr. water on ignition, 1.0602 gr. WO<sub>3</sub> and 0.1508 gr. ZnO = 17.16 p. ct. water, 72.52 p. ct. WO<sub>3</sub>, and 10.31 p. ct. ZnO.

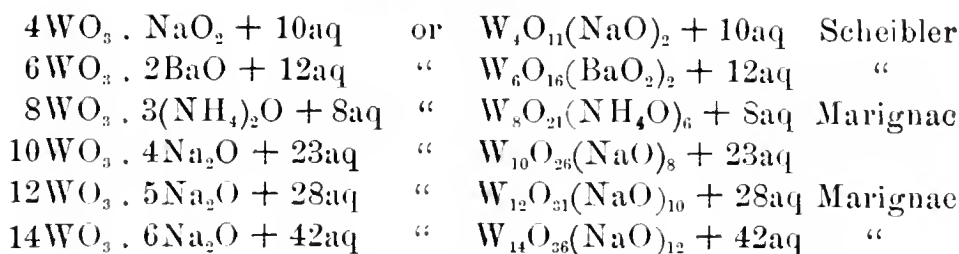
		Calc'd.	Found.
22WO <sub>3</sub>	5104	72.69	72.52
9ZnO	729	10.38	10.31
66H <sub>2</sub> O	1188	16.93	17.16
	<hr/> 7021	<hr/> 100.00	<hr/> 99.99

The salt was dried for some time upon woollen paper.

*General Conclusions.*—From my own investigations, as well as from those of other chemists who have preceded me, I arrive at the following classification of the alkaline tungstates as most nearly representing the present state of our knowledge. There are three series of salts, which may be termed respectively normal tungstates, metatungstates, and pyro-tungstates. The two first-named series may be represented by the following as typical salts:—

*Normal Series.*



*Meta-Tungstates.*

The salts of the normal series require no special notice. As already stated, I have not succeeded in preparing the di- and tri-salts of Lefort, but there seems to be no reason to doubt their existence. The pyro-salts are obtained from the meta-salts by ignition, as insoluble crystalline masses, which are decomposed by long boiling with water. All the meta-tungstates with an alkaline base, appear to contain water of constitution and to have an acid reaction, but it is difficult to determine the quantity of basic hydrogen with certainty, and the mere fact that the salts have an acid reaction is not in itself conclusive evidence that they are in the strict chemical sense *acid*. Tungstates have been described by different chemists which do not fall within either of the groups given above. In all these cases, however, it will be found on examination, that the analyses do not agree well with the formulas assigned, and that there is reason to believe that the salts studied were mixtures. I consider it at least probable that the tri-salts of Lefort belong in reality to the meta-series, their molecular weights being doubled. But it is of course possible that we have here cases of isomerism, and I much regret that I did not succeed in obtaining these salts for study and comparison. With respect to the double salt which I have described above, and which has the formula



I may remark that it is possible that the compound is really

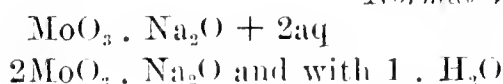


and that it is not a double salt, but one term in a series which we obtain by again doubling the formulas of the meta-tungstate as I have given them above. The question is one which I must leave undecided for the present at least.

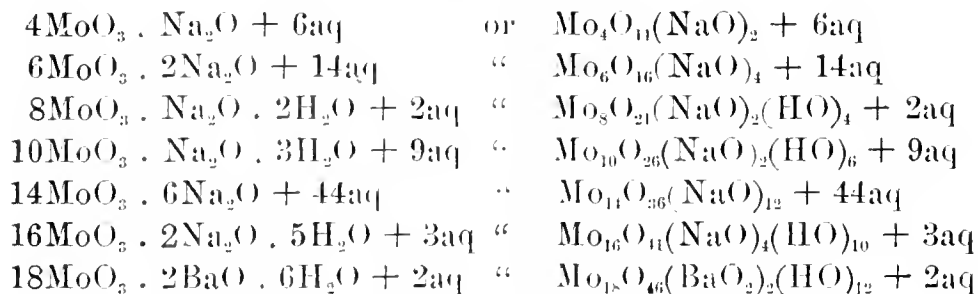
The analogy between the compounds of tungsten and

molybdenum is in general so great, that we ought to expect to find alkaline molybdates corresponding to the three series of tungstates. We owe to Ullik the most complete examination of the molybdates which has been published. A careful study of his results will show that, while we have a number of molybdates to which there are apparently no corresponding tungstates, we have at least reason to believe in the existence of the three series of normal, meta, and pyro salts. Thus the following salts may be assumed as typical:—

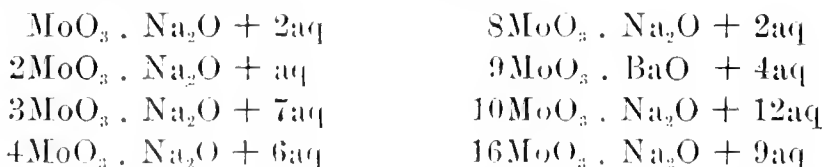
*Normal Series.*



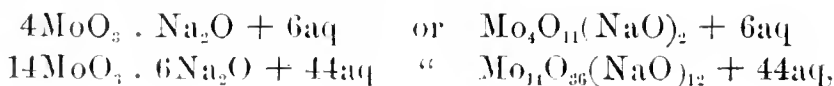
*Meta Series.*



It may of course be maintained that the arrangement of the acid salts of molybdic oxide which I have adopted is purely arbitrary, and that they might be written with equal or greater probability in the usual manner, as members of the normal series, which would then be:



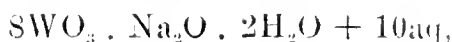
To this I reply that one arrangement is no more arbitrary than the other, since we have no positive knowledge of the constitution of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown. The commonly received view is therefore also a pure assumption. In any case, however, we have the two salts represented respectively by the formulas



forming the upper and lower limits of a molybdic series corresponding to alkaline tungstates, and from these we may fairly infer the existence of the intermediate compounds. But one acid tungstate of the meta series is at present known, the salt



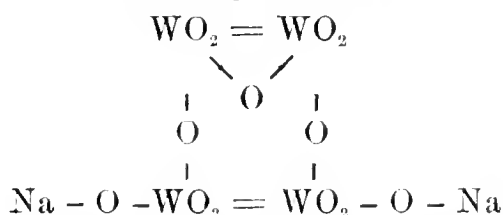
This may be considered as an acid salt of the 8-atom term, and written



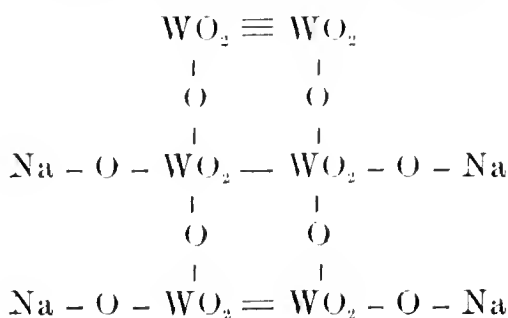
so that it will correspond with the molybdic salt



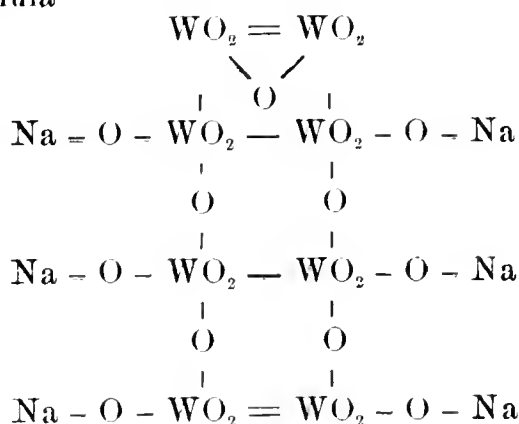
But the supposition that acid metatungstates of the 4 : 1 series really exist is in no way inconsistent with the view of the whole subject which I have taken. So far as I know, no attempt has been made to exhibit the mode of union of the elements in the higher tungstates. Our views of the subject will differ according as we consider tungsten as tetratomic or hexatomic. In what follows I have adopted the latter hypothesis, partly because the hexatomic character of tungsten is well marked in various compounds, as for example in  $\text{WCl}_6$ , and partly because the graphical representations are, on the whole, simpler. Moreover, if we consider tungsten to be tetratomic in the normal series, we obtain a reason for the existence and peculiar character of the meta series, by supposing that in this the metal is hexatomic. We may, to begin with, represent sodic metatungstate,  $4\text{WO}_3 \cdot \text{Na}_2\text{O}$ , as follows:



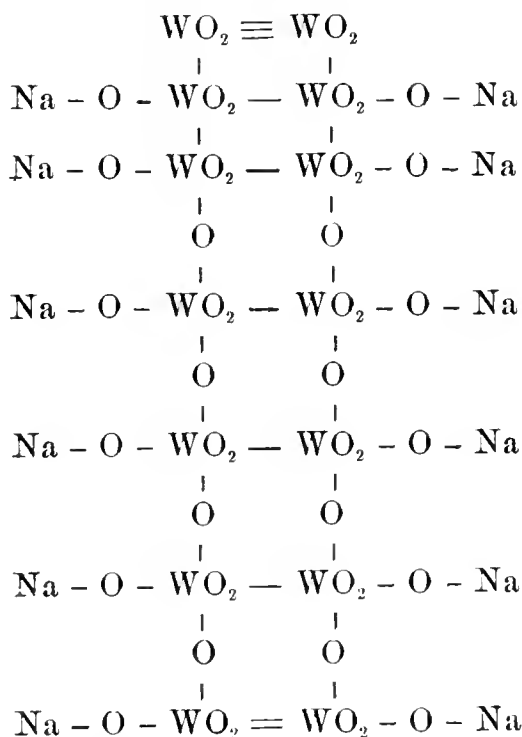
The next term in the series,  $6\text{WO}_3 \cdot 2\text{Na}_2\text{O}$ , will then be



The third term,  $8\text{WO}_3 \cdot 3\text{Na}_2\text{O}$ , may be represented by the graphical formula

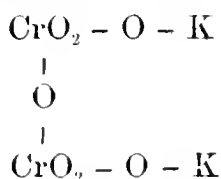


and so on for the other known terms, the highest,  $14\text{WO}_3 \cdot 6\text{Na}_2\text{O}$ , being represented by the expression



It will be seen that, with this view of the subject, those terms in the series in which the number of atoms of sodic oxide is even are represented by formulas in which the free atoms of  $\text{WO}_2$  are united, in part directly, and in part by oxygen, while the union is direct when the number of atoms of sodic oxide is odd. I shall return to this subject in speaking of the phosphotungstates and other complex inorganic

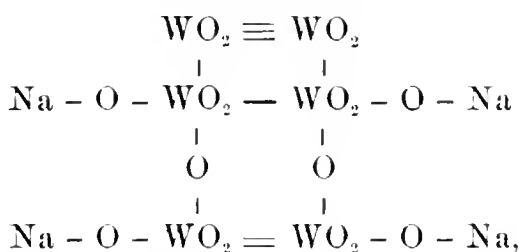
acids. No great value can, in the present state of our knowledge, be attributed to formulas like the above. They afford, however, some assistance in showing the possible mode of formation of the different terms of the series, but various other constructions may be devised which are perhaps equally probable. In adopting provisionally the particular construction which I have used, I have simply followed the clew given by the commonly received formula for potassic dichromate,



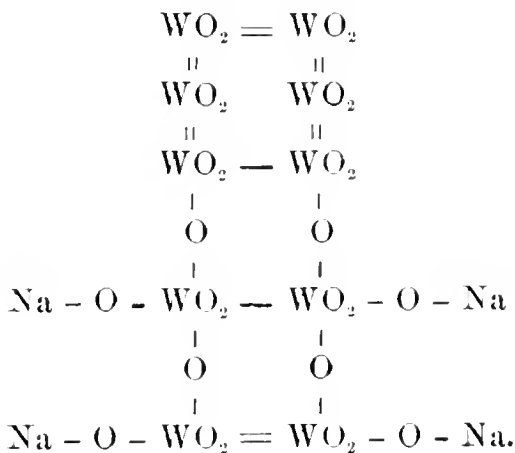
which of course gives a similar expression for the homologizing term in the acid tungstate series. So far as I am aware, no attempt has been made to formulate the remarkable compounds of tungsten described by Wœhler and others, and which may be expressed empirically by the formulas



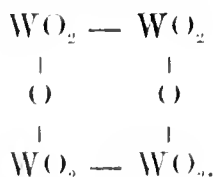
If we double these formulas, we may bring them into harmony with the series of acid tungstates by writing them respectively,



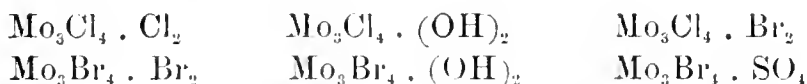
and



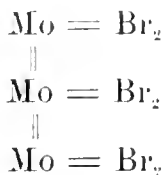
These formulas, if like the others purely hypothetical, have at least the merit of explaining the production of the insoluble sodium salts in a simple and natural manner. They are also entirely consistent with the simplest view which we can adopt with respect to the constitution of the blue oxide of tungsten, which is commonly written  $W_2O_5$ , but which is much more probably  $W_4O_{10}$ , and structurally



The progress of science tends to show that the constitution of inorganic compounds is more complex than would at first appear. It would not be difficult to multiply instances which support this view, but I shall content myself with citing a single case, which has not been discussed, and which, strangely enough, has attracted but little attention. I refer to the remarkable series of compounds of molybdenum studied by Blomstrand\* and by Atterberg.† Representative terms in this series are expressed by the formulas



omitting water of crystallization for greater brevity. The action of alkalis upon the bromide  $Mo_3Br_4 \cdot Br_2$  produces first  $Mo_3Br_4 \cdot (OH)_2$ , and afterward  $Mo_3(OH)_4(OH)_2$ , or  $Mo_3(OH)_6$ , the hydrate of the protoxyde of molybdenum, usually written  $MoO \cdot OH_2$ , or  $Mo(OH)_2$ . There is therefore good reason to believe that the lowest expression for this hydrate is  $Mo_3(OH)_6$ , the structural formula of the corresponding bromide being, perhaps



In this formula the end atoms of molybdenum are tetra-atomic, and the middle atom hexatomic, which will perhaps

\* Journal fuer prakt. Chemie, 82, 136.

† Nagra bidrag till K nnedomen om Molybden, Stockholm, 1852, p. 16.

explain the fact that there are but two movable atoms of bromine in a whole series of salts. If molybdic protoxide is  $\text{Mo}_3\text{O}_3$ , it is probable that the teroxide is not  $\text{MoO}_3$ , but rather some higher multiple of this expression, and we may extend the inference to  $\text{WO}_3$  also.

With these preliminaries, I pass to the special subject of my work.

[To be continued.]

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## CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

### No. II.

## ON SOME COMPOUNDS OF AROMATIC AMINES WITH SILVER NITRATE AND SULPHATE.

BY W. G. MIXTER.

A few compounds of silver nitrate with amido substances in the benzol series have been made, but no special importance appears to have been attached to them. Griess\* found that one molecule of azodiphenyl-diamine united with silver nitrate to form  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{AgNO}_3$ , and he also obtained the azobromodiphenyl-diamine product  $\text{C}_{12}\text{H}_9\text{Br}_2\text{N}_3\text{AgNO}_3$ . Hofmann† found that two molecules of melaniline united with one molecule of silver nitrate.

It seemed an object to prepare some compounds with the aromatic monamines, and the following are some of the results.

### *Aniline Silver Sulphate.*

5 grams of silver sulphate and 6 grams of aniline were dissolved in boiling water. Some silver was reduced, and there was a dark residue. The filtrate from the hot solution

\* Liebig's Ann. 121, 257.

† Liebig's Ann. 67, 129.

gave on cooling a mass of hair-like rose-tinted crystals, whose color was probably due to the reddish tint of the mother liquor. The product was washed with water and dried to a constant weight over caustic potash. The analysis shows a compound corresponding to silver sulphate with four molecules of aniline and two molecules of water.

		Calculated for (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>4</sub> Ag <sub>2</sub> SO <sub>4</sub> , 2H <sub>2</sub> O.	Found.
C	...	40.00	39.82
H	...	4.45	4.56
N	..	7.78	7.73
Ag	...	30.00	30.06
S	...	4.44	4.47
O	...	13.33	...
		<hr/> 100.00	

The substance lost *in vacuo* over oil of vitriol in four days 33.08 p. ct. Two molecules each of aniline and water are equal to 30.83 p. ct. Absolute alcohol removes the larger portion of aniline from the aniline silver sulphate and leaves a residue which reacts for aniline. A product from commercial aniline thus treated left a residue in which the silver found was 53 p. ct. C<sub>6</sub>H<sub>7</sub>NAg<sub>2</sub>SO<sub>4</sub> has 53.3 p. ct. of silver.

*Paratoluidine Silver Sulphate.*

6 grams of solid toluidine and 4.5 grams of silver sulphate gave by the method above described an analogous compound of the same appearance as the aniline silver sulphate.

		Calculated for (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> ) <sub>4</sub> Ag <sub>2</sub> SO <sub>4</sub> , 2H <sub>2</sub> O.	Found.
C	...	43.30	43.02
H	...	5.15	5.22
N	...	7.22	7.14
Ag	...	27.83	27.79
S	...	4.12	4.16
O	...	12.38	...
		<hr/> 100.00	

Absolute alcohol removes all the toluidine from the substance and leaves silver sulphate.

*Metanitriline Silver Nitrate.*

13 grams of metanitriline (m. p.  $110^{\circ}$  C) were dissolved in boiling absolute alcohol, and added to a boiling solution of 2 grams of silver nitrate in absolute alcohol. The slight precipitate which formed was filtered off and the solution was rapidly cooled. The mass of hair-like yellow crystals was washed with absolute alcohol and dried over oil of vitriol.

		Calculated for ( $C_6H_4NO_2NH_2$ ) $_4$ AgNO $_3$ .	Found.
C	...	39.89	39.72
H	...	3.32	3.43
N	...	17.45	17.35
Ag	...	14.96	15.11
O	...	24.38	...
		<hr/> 100.00	

Metanitriline silver nitrate melts without decomposition at  $124^{\circ}$ – $125^{\circ}$  C. Cold water completely removes the silver nitrate and leaves metanitriline.

*Nitrotoluidine Silver Nitrate.*

8 grams of nitrotoluidine (m. p.  $77.5^{\circ}$ ) were dissolved in boiling water, and a solution of 2.5 grams of silver nitrate was added; the small black decomposition product was filtered off and the solution cooled. The greenish-yellow crystalline product was washed with water, and dried over oil of vitriol.

		Calculated for ( $C_7H_6NO_2NH_2$ ) $_4$ AgNO $_3$ .	Found.
C	...	43.20	42.81
H	...	4.11	4.28
N	...	16.19	16.06
Ag	...	13.88	13.98
O	...	22.62	...
		<hr/> 100.00	

The substance melts without decomposition at  $131^{\circ}$ – $132^{\circ}$ C., and is soluble in absolute alcohol. Its aqueous solution evaporates spontaneously in light without decomposition, and paper

saturated with it is not darkened by sunlight. Equal weights of silver nitrate and nitrotoluidine gave the same compound.

*Paratoluidine Silver Nitrate.*

A hot clear aqueous solution of solid toluidine was gradually added to a cold solution of silver nitrate, which was constantly agitated and kept cold to prevent decomposition. The almost white crystalline product was washed with water.

		Calculated for (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> ) <sub>2</sub> AgNO <sub>3</sub> .	Found.
C	...	43.75	43.52
H	...	4.68	4.79
N	...	10.94	10.85
Ag	...	28.13	28.17
O	...	12.50	...
		<hr/>	
		100.00	

It melts with decomposition at 101°C. When treated with absolute alcohol it slowly decomposes with the separation of a brownish mass.

From 6 grams of a liquid marked  $\beta$ -toluidine and 2 grams of silver nitrate a product was obtained which gave no formula.

		Calculated for (C <sub>7</sub> H <sub>7</sub> NH <sub>2</sub> ) <sub>4</sub> AgNO <sub>3</sub>	Found.
C	...	56.19	53.89
H	...	6.02	5.94
N	...	11.71	...
Ag	...	18.06	19.88
O	...	8.02	...
		<hr/>	
		100.00	

The atomic ratio of the carbon to the hydrogen is as 7 to 9.27, corresponding within the limits of the errors of analysis to that of toluidine. Another experiment gave similar results. The quantity of liquid toluidine at command was too small to test its purity. It boiled at 195°–198° C. The results indicate that the liquid toluidine contained some of the solid modification, and that the substance analyzed was a mixture of (C<sub>7</sub>H<sub>7</sub>NH<sub>2</sub>)<sub>4</sub>AgNO<sub>3</sub> and (C<sub>7</sub>H<sub>7</sub>NH<sub>2</sub>)<sub>2</sub>AgNO<sub>3</sub>.

Aniline silver sulphate  $(C_6H_5NH_2)_4Ag_2SO_4, 2H_2O$ .

Paratoluidine silver sulphate  $(C_7H_7NH_2)_4Ag_2SO_4, 2H_2O$ .

Metanitraniline silver nitrate  $(C_6H_4NO_2NH_2)_4AgNO_3$ .

Nitrotoluidine silver nitrate  $(C_7H_6NO_2NH_2)_4AgNO_3$ .

Paratoluidine silver nitrate  $(C_7H_7NH_2)_2AgNO_3$ .

The first two compounds without the water of crystallization, are analogous to the ethylenediamine\* and the ammonia compounds of silver sulphate; the paratoluidine silver nitrate is similar to  $(NH_3)_2AgNO_3$ . The nitraniline silver nitrate and the toluidine silver nitrate contain one more ammonia group than was known to join to silver nitrate, and it is worthy of notice that nitraniline and toluidine are weak bases. In making the five bodies, excepting the nitraniline silver nitrate, an excess of the silver salt was used, hence the work does not decide whether more molecules of these amines will join a molecule of the silver salts. When ammonia is added to solutions of silver sulphate and of silver nitrate, a precipitate forms at first; but the five amines when added to an excess of the silver salts in dilute solutions, do not cause turbidity even after some hours, except in case of the toluidine, which at first produces no turbidity, but slowly gives a brown precipitate. This reaction, and the fact that two of the bodies are completely separated by simple solvents into the constituents from which they were made, indicate that the substances are "molecular compounds," similar to hydrous salts. The writer is aware that the constitution of a large number of bodies resulting from the union of ammonia or amines with metallic salts, can best be explained by supposing that the metal is joined to pentad nitrogen, and that the nitrogen atoms join each other. The present theory of valence does not explain the constitution of double salts or of hydrous salts, and there is no proof as yet that it explains the ammonia and amine addition products with metallic salts.

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\*Am. Jour. 17. 427.

## No. III.

ON CLARKE'S METHOD FOR THE SEPARATION  
OF TIN FROM ARSENIC AND ANTIMONY.

BY FRED. P. DEWEY.

In the beginning of the year 1876 an investigation was undertaken on the separation of tin, arsenic and antimony. After some study on the published methods and some work on a few of them, it was decided to make a thorough investigation of the method proposed by F. W. Clarke,\* as that seemed the most favorable method notwithstanding the poor results obtained by G. C. Wittstein.† Clarke's method is to add to the solution of the metals prepared as for the precipitation of sulphides, oxalic acid in the proportion of twenty parts to one part of tin, keeping the solution so concentrated that oxalic acid will separate in the cold. Hydrogen sulphide gas is then passed through the boiling solution until the antimony and arsenic are all precipitated, the solution is allowed to stand in a warm place for half an hour, the sulphides are filtered off and separated according to any of the well-known methods; the filtrate is neutralized by ammonia, the precipitate formed dissolved in ammonium sulphide, and acetic acid added in excess, whereby the tin is precipitated as a light colored mixture of sulphide and oxide which soon darkens in color. When complete precipitation is insured by standing in a warm place several hours, it is filtered off, washed in ammonium nitrate solution, ignited and weighed as stannic oxide,  $\text{SnO}_2$ . The results given by Clarke were the recovery of 99.93 and 99.57 p. ct. of the tin from solutions containing unknown amounts of antimony and arsenic, the latter result being considered poor by him, and owing to incomplete precipitation from filtering too soon after the addition of reagents. It was originally intended to investigate the separation of tin from antimony, and tin from arsenic separately, and then tin from antimony and arsenic; but it soon became evident that with the time at my disposal I could only undertake the

\* *Am. Jour. Sci.* 49, 145† *Fresenius' Zeitschrift*, 9, 487.

separation of tin from antimony, and the experiments here described were devoted entirely to that object.

I made two separations, intending to follow Clarke's plan exactly. Pure metallic antimony was weighed out and dissolved in strong hydrochloric acid with the addition of potassium chlorate. As soon as all the antimony had gone into solution, weighed amounts of pure metallic tin were added, and the final solution evaporated to dryness to drive off hydrochloric acid and decompose all potassium chlorate; the residue was taken up in a few drops of hydrochloric acid and water, and the requisite amount of oxalic acid added. As oxalic acid is soluble in ten parts of cold water\*, one solution could not be over 55 cc. and the other over 39 cc., no account being taken of the few drops of hydrochloric acid added. Hydrogen sulphide was transmitted through the boiling solution for half an hour, when the antimony seemed to be all down. After standing for half an hour in a warm place, a portion of the fluid was run through a weighed filter, and the filtrate tested with hydrogen sulphide, when more antimony came down; this was filtered off and the second filtrate tested, when still more antimony came down. Thereupon I gave up the idea of keeping the solution so concentrated, and diluted it a little, when the antimony came down so that on testing the filtrate by diluting and adding more hydrogen sulphide no antimony was precipitated; the precipitate was filtered off, washed well, dried at 100°C. and weighed. The filtrate was diluted largely, ammonia added, the slight precipitate dissolved in ammonium sulphide, acetic acid added in excess, and the whole allowed to stand over night, when the precipitate was filtered off, washed in ammonium nitrate, ignited and weighed as stannic oxide,  $\text{SnO}_2$ .

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.3089 gr.	0.2722 gr.	0.3063 gr.	0.2704 gr.
0.2671 "	0.1908 "	0.2704 "	0.1821 "

In a second set a portion of the antimony trisulphide was heated to 230°C. in a tube filled with dry carbon dioxide and the loss calculated for the whole precipitate.

\* Storer's Dict. of Solubilities.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.1542 gr.	0.2705 gr.	0.1356 gr.	0.2717 gr.
0.1172 "	0.3736 "	0.1186 "	0.3760 "

Some qualitative experiments were undertaken to test the influence of free hydrochloric acid on the separation, and also the statement of Clarke that antimony could not be detected in the filtrate from the antimony trisulphide either by the Marsh test or the black stain on platinum with zinc, and that oxalic acid did not interfere with either of these tests. I found that oxalic acid obscured the platinum and zinc test by the formation of a dense white coating on both the platinum and zinc when the acid became nearly neutralized, (probably an oxalate of zinc) which completely masked any black stain that might have been produced on the platinum, but that it did not obscure the Marsh test in the least. Five solutions were prepared as before, each solution containing 0.2 gr. tin and 0.15 gr. antimony, and evaporated to dryness, the residues being taken up in oxalic acid; and, starting with no free hydrochloric acid, 1, 3, 5 and 7 cc. of hydrochloric acid of 1.09 sp. gr. were respectively added. These solutions were diluted to 250 cc. Hydrogen sulphide was transmitted through the boiling solutions for three-quarters of an hour, and the antimony trisulphide filtered off. The filtrates were tested in an ordinary Marsh apparatus.

No. 1 containing no HCl gave only a slight yellowish mirror, probably S.

No. 2 containing 1 cc. HCl gave a metallic mirror for about two minutes.

No. 3 containing 3 cc. HCl gave a good metallic mirror for some time.

No. 4 containing 5 cc. HCl gave a very good metallic mirror for a long time, about equal portions of the filtrates being used for each test.

No. 5 containing 7 cc. HCl deposited thin red flakes of  $\text{Sb}_2\text{S}_3$  on concentration.

These results show, that to get the best separation no hydrochloric acid can be present, although a very small amount can be present without exerting any very great solv-

ent action on the antimony trisulphide.\* The precipitates of antimony trisulphide were dissolved in strong hydrochloric acid, evaporated and treated with zinc; the metallic precipitates were treated with small amounts of dilute hydrochloric acid, filtered, and the filtrates tested with mercuric chloride, when heavy precipitates of mercurous chlorides came down in every case. These results show that it is always necessary to make double precipitations of the antimony, a point suggested by Clarke as being necessary only when great accuracy is required. The results of the above described experiments indicate that the following modifications of the original plan are required, viz: a solution *without free mineral acids*, and diluted to 250 cc. for 0.2 gr. of each metal; also in all cases a double precipitation of the antimony.

Solution in hydrochloric acid with potassium chlorate being rather tedious, a mixture recommended by Dr. Clemens Winkler in Fresenius' *Zeitschrift*, consisting of one part strong nitric acid, four parts strong hydrochloric acid, and five parts water, was tried and found very satisfactory. The evaporation of a solution of tin and antimony prepared by this mixture cannot safely be undertaken, on account of the well known fact that stannic chloride will volatilize from a dilute acid solution, and both stannic chloride and antimony trichloride from a concentrated acid solution on evaporation, and the use of an alkali to neutralize the acid is objectionable for reasons I shall state beyond; but, from the fact that in the analyses given the metals were dissolved in hydrochloric acid and potassium chlorate and evaporated to dryness without any very great loss on the total amount of metals used, it suggested itself that the presence of a sufficient amount of potassium chloride to form double salts with all of the tin and antimony used, would serve to fix the tin and antimony during evaporation. Two experiments were made to ascertain definitely whether tin or antimony would volatilize under such conditions. 1.7 gr. of tin were dissolved in 50 cc. of the aqua regia and 2.5 gr. of potassium chloride were added; the solution was transferred to a retort of 350 cc. capacity, diluted to 100 cc. and distilled at about 100°C. in an air bath, while a slow

\*The poor results obtained by Wiltstein were probably due to the presence of large amounts of free acid in his solutions.

current of air was forced through the retort. When half of the fluid had passed over, the receiver was removed, emptied and returned, then the distillation was resumed. The distillate was diluted to 100 cc., part of the acid was neutralized by sodium carbonate, and hydrogen sulphide was transmitted through it, when there was only a slight separation of sulphur, probably caused by chlorine given off from the aqua regia. The distillation was carried to dryness, the distillate treated in the same way and with the same result. A second portion of tin was treated in the same way omitting the addition of potassium chloride, and in each portion of the distillate, heavy precipitates of tin sulphide were obtained. 1.5 gr. of antimony were treated exactly as the tin in the first experiment with the same result. 1.5 gr. more of antimony were treated without potassium chloride. In the first distillate containing three-quarters of the liquid no antimony could be detected, but in the final distillate a large amount of antimony was found. These experiments show that solutions of stannic chloride and antimony trichloride containing free hydrochloric or nitric acid or both, can be safely evaporated to dryness if a sufficient amount of potassium chloride is present. In all of my subsequent analyses the free acid was removed by evaporation to dryness in the presence of an excess of potassium chloride.

The course next adopted was to dissolve about 0.2 gr. of each metal in the aqua regia, add sufficient potassium chloride and evaporate to dryness. The requisite amount of oxalic acid was then placed in the beaker and boiling water added until a clear solution was obtained, which is very easy to do. The solution was diluted to 250 cc. Hydrogen sulphide was transmitted through the boiling solution for half an hour. The precipitate was immediately filtered off\* and washed. The precipitate of antimony trisulphide containing a little tin sulphide was dissolved in ammonium sulphide. This solution was poured into a boiling solution of oxalic acid, containing enough of the acid to decompose the ammonium sulphide, and still have sufficient excess to hold the tin in solution.

\* It was observed that when the fluid with the  $Sb_2S_3$  precipitate was allowed to stand to remove  $H_2S$ , there was always a separation all through the liquid of flakes which did not look like S, but did look like  $SnS_2$ ; a supposition supported by the fact that these flakes separated in the filtrate from  $Sb_2S_3$ , filtered off immediately, as it cooled during filtering, and were dissolved again on applying heat.

Hydrogen sulphide was transmitted through the boiling solution for ten minutes, and the solution filtered through a weighed filter; the precipitate was well washed with hot water, dried at 100° C., weighed and a portion converted into pure anhydrous antimony trisulphide as before. The filtrates containing the tin were united and treated with the proper reagents; the precipitate was filtered off after standing, washed in ammonium nitrate and weighed as tin oxide. Each filtrate was always tested to insure complete precipitation.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.2243 gr.	0.2238 gr.	0.2390 gr.	0.2218 gr.
0.1908 "	0.2346 "	0.2058 "	0.2219 "
0.3871 "	0.2573 "	0.3949 "	0.2607 "
0.3108 "	0.2187 "	0.3158 "	0.2203 "

Repeated testings of the weighed tin and antimony indicated that the actual separations were satisfactory. There were, however, some difficulties and some obvious sources of error in the methods used for their determination which would cause gain of antimony and gain or loss of tin. On dissolving the antimony sulphide in strong hydrochloric acid, a black residue was always obtained, no matter how much the precipitate had been washed, indicating the presence of oxalic acid in the precipitate in some form. The solution of tin required extreme dilution to get it all down, the solution being diluted in one case to nearly 1500 cc., which seemed to be due to the unavoidable presence of large amounts of ammonium oxalate. Besides this the washing of the tin precipitate was very difficult and tedious indeed, which is a reason for keeping the amount of salts in the solution as small as possible.

To avoid the difficulty of precipitating the tin completely and washing it thoroughly, it seemed necessary to remove the oxalic acid entirely from the filtrates containing it. Strong sulphuric acid was decided upon as the best means, that is to evaporate the solution to dryness, and treat with strong sulphuric acid at about 100° C., which rapidly decomposes the oxalic acid into water, carbon monoxide and dioxide. In two experiments 0.5 gr. tin were dissolved in the aqua regia, potassium chloride was added, the solutions were evaporated

to dryness and the residues taken up in oxalic acid, 25 gr. in one and 30 gr. in the other. They were again evaporated to dryness and treated with about 40 cc. of strong sulphuric acid at 100° C. until all effervescence had ceased, when they were diluted to 500 cc., treated with hydrogen sulphide gas for half an hour and allowed to settle, after which the precipitates were filtered off, washed in ammonium nitrate and weighed as tin oxide, yielding 0.4998 and 0.4996 gr. tin. Applying this process to the filtrate from the antimony trisulphide, the following separations were next made, the process being conducted as before except the dilution of the solution before the precipitation of the antimony trisulphide to 400 cc., when 0.5 gr. of each metal were used.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.2000 gr.	0.2000 gr.	0.2084 gr.	0.1964 gr.
0.2000 "	0.2000 "	0.2030 "	0.2031 "
0.3000 "	0.3000 "	0.3070 "	0.3029 "
0.5000 "	0.5000 "	0.5066 "	0.5004 "
0.5000 "	0.5000 "	0.5177 "	0.4962 "

The last two antimony results were corrected for the carbonaceous residue, which was filtered off on a small filter and weighed, being 0.0085 and 0.0070 gr. Following the analogy of the two cases, we may suppose, as J. P. Cooke, jr.,\* does in his determination of the atomic weight of antimony, that this residue comes from occluded oxalic acid.

A slight modification of Bunsen's† method of weighing antimony as antimony tetroxide having given 0.4996 and 0.4986 gr. antimony instead of 0.5000 gr., four separations were made in which the antimony was weighed as antimony tetroxide, the other details remaining as before.

Used.		Found.	
Sb.	Sn.	Sb.	Sn.
0.5000 gr.	0.5000 gr.	0.5190 gr.	0.4911 gr.
0.5000 "	0.5000 "	0.5067 "	0.4963 "
0.5000 "	0.5000 "	0.5136 "	0.4973 "
0.5000 "	0.5000 "	0.5146 "	0.4926 "

\*Transactions of Amer. Acad. of Sci., Bost., 13, 15.

† Ann. der Chemie, 106, 3.

While the results obtained by this method are no better than those obtained by weighing antimony as trisulphide, yet it required less time and is a much neater operation to get them.

Since reaching the above results and conclusion Bunsen\* has published further experiments on this method of weighing antimony, and reaches the conclusion that it cannot easily be done with accuracy, because more oxygen than is necessary will be driven off at a temperature only slightly above that required to convert antimony pentoxide into the tetroxide, and at a very intense heat the trioxide thus formed will be volatilized. From my results it would seem that the heat employed was too low rather than too high.

In conclusion, I desire to express my thanks to Prof. O. D. Allen for much kind assistance during the progress of the above work.

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#### NO. IV.

### INFLUENCE OF ACETIC ACID ON THE SEPARATION OF IRON AS A BASIC ACETATE FROM MANGANESE, ZINC, COBALT AND NICKEL.

BY JOHN JEWETT.

It has often been observed when manganese is separated from iron by precipitating the latter as a basic ferric acetate, that some manganese is carried down with the iron precipitate. Eggertz,† calling attention to this fact, stated that this trouble could be obviated, at least to a great extent, by the presence of free acid. To this end he recommends adding to a volume of 500 cc., after nearly neutralizing with sodium carbonate, 3 cc. of HCl (strength not given). Stöckmann communicated in Fresenius' *Zeit.* 1877, p. 172, the results of a series of experiments in separating iron from manganese in "Spiegeleisen" containing about 10 p. et. of manganese. He found that varying, and, usually, very considerable amounts of manganese were precipitated along with the iron, in many

\* Fresenius' *Zeitschrift*, 18, 268.

† Berg- und Huettenmännische Zeitung, 1867, p. 187.

cases equalling 10 p. ct. of all that was present, and concludes that it is absolutely necessary to redissolve and reprecipitate the iron and recover the manganese in the second filtrate. He alluded to the modification recommended by Eggertz, but did not adopt it, finding the free acid made the iron precipitate difficult to wash. C. Krämer\* was astonished at these results, and states that the only precaution necessary (besides thorough washing) is the addition of one or two drops of dilute acetic acid to the previously neutralized solution, before adding sodium acetate and boiling; he found that at most only  $\frac{1}{10}$  p. ct. of manganese goes down with the iron. The experience of G. Matzurke† was, on the other hand, quite like that of Stöckmann. He found, contrary to Krämer, that the addition of one or two drops of dilute acetic acid made no appreciable difference in the results.

In view of these statements concerning a much used process, I have, with the advice of Prof. O. D. Allen, made some experiments to ascertain the influence of free acetic acid in this method of separating iron from manganese and the other metals, zinc, cobalt and nickel. As a basis of operation, solutions of  $\text{Fe}_2\text{Cl}_6$  containing free  $\text{HCl}$ , and of  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$  and  $\text{Ni}(\text{NO}_3)_2$  of known strength, (.2 gr. of the metals to every 100 cc. of solution) were made; then by uniting 100 cc. of the iron solution with the same amount of any one of the other solutions, a mixture of the desired metals to be separated was obtained. A few preliminary trials with iron and manganese gave results in accordance with the statements of both Stöckmann and Eggertz. Presence of free acid decreased the amount of manganese in the iron precipitate, but *too much* prevented complete precipitation of the iron. To ascertain to what extent free acetic acid is efficient in keeping manganese, likewise zinc, nickel and cobalt in solution, when present in quantities not too great to prevent precipitation and washing of the iron, necessitated a series of experiments, in which the only variable factor was the acetic acid. In every case, 2 gr. sodium acetate were used (an amount equal to ten times the weight of iron present), and the solutions were diluted to the same volume, viz: 300 cc. before boiling to separate iron. The precipitated iron was examined after thorough washing,

\* Fresen. Zeit. 1877, p. 334.

† Fresen. Zeit. 1878, p. 78.

by redissolving and repeating the separation, and testing the filtrate from the iron precipitate, according to whether Mn, Zn, Co or Ni was present, with Br,  $\text{NaCO}_3$  or  $\text{NaOH}$ . The results are here tabulated :

P. ct. by volume of Acetic Acid (1.044 Sp. Gr.) added.	Taken Fe .2 gr. " Mn .2 "	Taken Fe .2 gr. " Zn .2 "	Taken Fe .2 gr. " Ni .2 "	Taken Fe .2 gr. " Co .2 "
	P. ct. of Mn in 2d Filtrate.	P. ct. of Zn in 2d Filtrate.	P. ct. of Ni in 2d Filtrate.	P. ct. of Co in 2d Filtrate.
0	2.788	...	...	...
$\frac{1}{2}$	.697	2.849	1.888	...
1	.585	2.046	1.770	.590
2	.193	...	1.652	...
3	.154	...	1.468	...
4	Trace	0	1.219	.315
4	Trace	0	...	...
5	Trace	...	.314	...

It was found that 4 p. ct. by volume of acetic acid 1.044\* sp. gr. has no appreciable bad effect on the separation and filtration of the iron; when 5 p. ct. is used its effect is sometimes apparent, but occasions no great trouble. On making some trials with over 5 p. ct., iron was not always completely precipitated, and was very difficult to wash. Great care was taken in these experiments to have as little free acid as possible present besides that intentionally added. This end can best be attained by adding sodium carbonate to the *cold* and preferably concentrated acid solution until a slight precipitate forms, which no longer redissolves by shaking and allowing to stand three or four minutes, but imparts a turbidity to the deep red solution;  $\text{HCl}$  must then be added without longer delay, drop by drop, until the fluid, though still dark, becomes clear. After neutralizing in this manner, the amount of acetic acid required to form the desired percentage of the final volume was added, next sodium acetate, and lastly the solution was diluted to the final volume (viz: 300 cc.) before boiling. Long boiling of the precipitate was avoided, one or two minutes sufficing to make the basic acetate settle quickly after removing the heat. The precipitate was washed with

\*This acetic acid, by volumetric determination, was found to contain 33.16 p. ct.  $\text{C}_2\text{H}_4\text{O}_2$ .

nearly boiling water, to which 2 gr. sodium acetate and 1 cc. acetic acid, per litre, had been added, until  $\text{AgNO}_3$  gave no reaction with the washings.

It may be concluded from the results shown in the table, that by using 4 p. ct. by volume of acetic acid, 1.044 sp. gr., and adhering to the above precautions, a complete separation by one precipitation can be obtained of zinc, and one sufficiently accurate for most purposes of manganese; while the amount of nickel and cobalt that goes down with the iron lessens with increase of acetic acid. The following quantitative separations of iron from zinc and manganese were also made. Precipitation was effected in a volume of 300 cc. containing 12 cc. acetic acid, *i. e.* 4 p. ct. of this volume, and 2 gr. sodium acetate.

Fe taken.	Zn taken.	Mn taken.	Fe found.	Zn found.	Mn found.
.1966 gr.	.1997 gr.	...	.1995 gr.	.1994 gr.	...
.2000 "	.2000 "	...	.1998 "	.1999 "	...
.1996 "	...	.2000 gr.	.1983 "	...	.2002 gr.
.2000 "	...	.2000 "	.1993 "	...	.2001 "

#### *Other Variable Conditions.*

A volume less in proportion to the iron present may doubtless be advantageous when large quantities of iron are to be precipitated. The writer, however, would not recommend, on account of increased difficulty of washing, less than 100 cc. per .1 gr. Fe.

Experiments made by E. H. Smith in this laboratory, on the separation of iron from manganese, under exactly the same conditions as described, except that double the amount of sodium acetate was used, gave essentially the same results.

He further ascertained that iron could not be precipitated in presence of a larger amount of acetic acid by increasing the amount of sodium acetate.

Since solutions containing free acid may be neutralized with ammonia or ammonium carbonate instead of sodium carbonate, when the presence of ammonium salts is not objectionable, for example in separating nickel from iron, I have duplicated

some of the above experiments with nickel, with no other change than the addition of ammonium chloride. The results are appended, showing the difference when  $\text{NH}_4\text{Cl}$  is present :

P. ct. by volume of acetic acid (1.044 sp. gr.) added.	P. ct. of Ni in 2d Filtrate.	P. ct. of Ni in 2d Filtrate, when 5 gr. $\text{NH}_4\text{Cl}$ were added.	Difference.
1	1.770	.904	.866
3	1.468	.708	.760
4	1.219	.511	.708

## ON THE ACTION OF IODINE MONOCHLORIDE UPON AROMATIC AMINES.

BY A. MICHAEL AND LEWIS M. NORTON.

The action of iodine monochloride on aromatic compounds was first investigated by P. Schuetzenberger\* in 1861. He produced mono- and di-iodobenzene by the action of this reagent on sodium benzoate. Soon afterwards, Schuetzenberger and Sengenwald† obtained an iodonitrobenzene by the action of iodine chloride on sodium nitrobenzoate, and they also prepared mono- and di-iodophenol by its action on phenol. Later, Schuetzenberger‡ obtained tri-iodophenol by treating phenol with a large excess of the reagent. In 1864, J. Stenhouse§ investigated the action of iodine monochloride on some aromatic bodies. He obtained tri-iodo-orcin by its action on orcin. Lately,|| tri-iodoresorcin was made in the same manner from resorcin. Stenhouse, in his research, investigated the behavior of iodine chloride toward the salts of

\* Rep. Chim. pure, 3, 145. † Rep. Chim. pure, 4, 144. ‡ Bull. Soc. Chim. [2], 4, 102.  
§ J. Chem. Soc. [2], 2, 327. || Ber. d. chem. Gesell. 1876, 1752.

aniline. He obtained a compound from whose proximate analyses he was unable to deduce a satisfactory formula, and he believed that this compound belonged to a new class of organic iodo-compounds. This body will be shown to be identical with tri-iodoaniline, which will be later described.

We have undertaken a new investigation of the action of iodine monochloride upon aromatic amines. It seemed probable that by the action of this compound higher substitution products could be obtained, than by the action of iodine on the amines.

The iodine chloride we employed in this investigation was prepared by passing a stream of dry chlorine over iodine, until the weight of the iodine had increased in the ratio of 1 mol. chlorine to 1 mol. iodine. Iodine chloride, so produced, is a dark red liquid, which solidifies at about  $10^{\circ}$ ; and which can be kept several weeks, without undergoing decomposition, when collected in tightly stoppered bottles.

The reagent was used in the form of vapor. A flask containing the iodine chloride was placed in a hot water bath, and connected with another flask containing a solution of the compound to be acted upon, and a current of dry air passed through the apparatus by means of an aspirator.

#### *Action of Iodine Chloride upon Acetanilide.*

The acetanilide was dissolved in a large excess of glacial acetic acid, and iodine chloride passed into the solution in the ratio of 1 mol.  $\text{ICl}$  to 1 mol.  $\text{C}_6\text{H}_5\text{NO}$ . The color of the solution became dark; after standing some hours a copious precipitate, consisting of iodoacetanilide, separated; and the filtrate contained a further quantity, which was precipitated by the addition of water. The iodoacetanilide was thus obtained in the form of a dark colored, crystalline precipitate, and was easily purified by two crystallizations from water. The iodine determination resulted as follows: 0.1588 gr. of substance gave 0.1426 gr. of  $\text{AgI}$ .

	Calculated for $\text{C}_6\text{H}_4\text{INH}(\text{C}_2\text{H}_3\text{O})$ .	Found.
1	48.65	48.53

When crystallized from water, iodoacetanilide forms white, rhombic plates, whose corners are frequently truncated. It

is slightly soluble in cold, but much more in hot water; alcohol and glacial acetic acid dissolve it very readily. The substance melts at  $181\frac{1}{2}^{\circ}$ .

Iodoacetanilide is easily converted by the action of hot, concentrated chlorhydric acid into the chlorhydrate of para-iodoaniline; if this is dissolved in water, and an excess of ammonia added, monoiodoaniline (melting point  $60^{\circ}$ ) is precipitated. The action of iodine chloride upon acetanilide is therefore analogous to that of chlorine or bromine, inasmuch as it furnishes a para-compound.

Para-iodoacetanilide is decomposed by warm concentrated nitric acid, and iodine is set free. A nitro-substitution product of iodoaniline can be obtained by dissolving the iodoacetanilide in a large volume of glacial acetic acid, adding an equal quantity of concentrated nitric acid, and heating a short time on a water bath. By partial neutralization the nitropara-iodoaniline is precipitated as a yellow crystalline mass, and is easily obtained in a pure state by repeated crystallizations from dilute alcohol. The iodine determination was as follows: 0.1639 gr. of substance gave 0.1470 gr. of AgI.

		Calculated for $C_6H_5IN_2O_2$ .	Found.
I	...	48.10	48.46

Nitropara-iodoaniline crystallizes from alcohol in long, dark yellow needles, which melt at  $122^{\circ}$ . It is insoluble in cold and nearly in hot water; easily soluble in alcohol and glacial acetic acid.

There is an important difference between the action of iodine chloride, and that of chlorine or bromine upon acetanilide; these elements form not only mono- but also di- and trichloro- and bromo-substitution products; while by the action of 2 or 3 mols. of ICl upon 1 mol. acetanilide, only the mono-iodo-compound is produced. The yield of iodoacetanilide is very satisfactory, reaching 85 per cent. of the amount required by the theory. According to Mills\* the yield of iodoaniline by the direct action of iodine on aniline is by no means large, and its production from iodoacetanilide may therefore be recommended.

\* Ann. der Chemie, 176. 354.

*Action of two Molecules of Iodine Chloride upon one Molecule of Aniline Acetate.*

The aniline was dissolved in a large excess of glacial acetic acid, and treated with the calculated amount of iodine chloride, the solution being carefully kept cool during the operation. The liquid became dark colored; and upon the addition of water, a black, partially crystalline mass separated, which was removed by filtration. By repeated crystallizations from alcohol, a nearly pure product was obtained, but it was found to be preferable to treat the black mass at once with steam, in the presence of caustic potash. The compound passes over very slowly, but is subsequently easily purified by a single crystallization from dilute alcohol. The analysis\* furnished the following numbers, which correspond to the formula  $C_6H_5I_2N$ :

0.2474 gr. of substance gave 0.1940 gr. of  $CO_2$  and 0.0440 gr. of  $H_2O$ . 0.1271 gr. of substance gave 0.1719 gr. of  $AgI$ . 0.5394 gr. substance gave 19.2 cc. of  $N$ . Bar. 776.5;  $t = 16^\circ$ .

		Calculated for $C_6H_5I_2N$ .	Found.
C	...	20.87	21.38
H	...	1.45	1.97
I	...	73.62	73.09
N	...	4.06	4.23
		100.00	

Di-iodoaniline crystallizes in long, white needles, which melt at  $95-95\frac{1}{2}^\circ$ , and solidify at about  $64^\circ$ . It is almost insoluble in cold water, and but sparingly soluble in hot; in cold alcohol moderately, in hot very easily soluble. It is somewhat soluble in glacial acetic acid and readily in acetic ether. Pure di-iodoaniline is easily carried over by steam, and the slowness with which it passes over in its first purification is due to the presence of foreign substances. Concentrated nitric acid attacks di-iodoaniline in the cold, probably forming a nitro-compound; hot nitric acid decomposes it with the liberation of iodine. Concentrated sulphuric acid blackens it in the cold, and decomposes it upon warming, with the evolution of iodine vapors.

\*The iodine determinations in this investigation were made according to the method of Carius. Chromate of lead was employed in the combustions. We have found it impossible to prevent traces of iodine from passing into the absorption apparatus, and for this reason the percentage of hydrogen obtained has usually been too high.

Di-iodoaniline possesses weak basic properties. A solution of di-iodoaniline in hot concentrated chlorhydric acid furnishes upon cooling the chlorhydrate, which separates in long, white needles, whose melting point it was impossible to determine, as they begin to decompose below 100°.

An analysis gave the following numbers: 0.3220 gr. of substance gave 0.1284 gr. of AgCl.

	Calculated for $C_6H_5I_2NHCl$ .	Found.
Cl	9.33	9.88

The chlorhydrate is easily decomposed by water into the free base and chlorhydric acid.

After the removal of the black mass, from which the di-iodoaniline was obtained, a quantity of white needles separated from the filtrate; these were found to consist of a mixture of mono- and di-iodoaniline. To effect the separation of the two bases, the precipitate was boiled with strong chlorhydric acid; upon cooling, a mixture of the two chlorhydrates separated. This was then treated with water; the chlorhydrate of mono-iodoaniline dissolved, while the salt of di-iodoaniline was decomposed into chlorhydric acid and the base, which remained undissolved. The separation is very complete.

*Action of three Molecules of Iodine Chloride upon one Molecule of Aniline Chlorhydrate.*

In order to obtain tri-iodoaniline we allowed 3 mols. of iodine chloride to act upon 1 mol. of aniline acetate. Numerous experiments showed that better results could be obtained by substituting a chlorhydric acid solution of aniline, in the place of the aniline acetate. The solution, on treatment with iodine chloride, became dark colored, and a black precipitate soon settled; as soon as the supernatant liquid became clear, this precipitate was removed by filtration. The filtrate was diluted with six times its volume of water, and allowed to stand twelve hours, during which time a mass of reddish colored needles separated. In order to purify this precipitate, it was boiled with a small quantity of glacial acetic acid, by which most of the impurities were removed. For further purification it was dissolved in hot alcohol, boiled twice with

animal charcoal, and then allowed to crystallize. The slightly colored crystals, thus obtained, were finally crystallized five times from alcohol. The analyses of the product, so purified, were as follows: 0.1383 gr. of substance gave 0.2093 gr. of AgI. 0.1092 gr. of substance gave 0.1624 gr. of AgI. 0.4185 gr. of substance gave 0.2398 gr. of  $\text{CO}_2$  and 0.0465 gr. of  $\text{H}_2\text{O}$ . 0.6064 gr. of substance gave 12.2 cc. of N. Bar. = 763mm.,  $t = 19^\circ$ .

		Calculated for $\text{C}_6\text{H}_3\text{I}_3\text{N}$ .	Found.	Found by Stenhouse. (Mean).	
C	...	15.28	15.62	15.66	
H	...	.86	1.23	1.07	
N	...	2.97	3.08	3.22	
I	...	80.89	81.75	80.35	63.23
		<hr/> 100.00			

Tri-iodoaniline crystallizes in long, white needles, which melt at  $185\frac{1}{2}^\circ$  without decomposition, and solidify at about  $146^\circ$ . It is insoluble in hot and cold water, slightly soluble in concentrated chlorhydric acid and also in cold alcohol. It is tolerably soluble in boiling alcohol; and, when the solution is slowly cooled, it crystallizes in long needles, which bear a striking resemblance to those of sublimed phthalic anhydride. Its best solvents are carbon disulphide and acetic ether, both of which dissolve tri-iodoaniline very readily, and glacial acetic acid, in which it is considerably soluble. It is volatile in a current of steam, but in less degree than the di-iodo-compound. The yield by the method described above is about 15 per cent. of the theoretical amount.

Tri-iodoaniline is not attacked by dilute nitric acid; concentrated acid dissolves it, forming a nitro-compound. Fuming nitric acid decomposes it in the cold, setting free iodine. Its behavior toward sulphuric acid is the same as that of di-iodoaniline. Tri-iodoaniline has no basic properties; it even crystallizes unchanged from concentrated chlorhydric acid.

We have already mentioned that Stenhouse obtained a beautiful crystalline body by the action of iodine monochloride upon aniline salts. The properties of this body coincide with those of tri-iodoaniline, and the analyses made by Stenhouse, whose mean we present, correspond, with the exception of the iodine estimations, well with those we obtained. In

order to remove all doubt, as to the identity of the two bodies, we have repeated the experiments of Stenhouse, and satisfied ourselves that they are identical.

*Action of Iodine Chloride on Metanitriline.*

By the direct action of bromine on metanitriline a tri-bromonitriline is formed. The analogy between the action of bromine, and that of iodine chloride on aniline led us to expect, that by the action of iodine chloride on metanitriline, a tri-iodo-compound would be produced; we therefore passed 3 mols. of iodine chloride into a solution of 1 mol. of nitriline in dilute chlorhydric acid. The solution, thus obtained, was allowed to stand several days, and then diluted with water. A yellow precipitate soon separated. This precipitate contained two compounds, which were separated in the following manner: the precipitate was dissolved in boiling alcohol; on cooling, one of the substances separated in long dark yellow needles, while the other substance remained in solution. The yellow needles were purified by repeated recrystallizations from alcohol, and analyzed with the following results: 0.2083 gr. of substance gave 0.2532 gr. of AgI. 0.4056 gr. of substance gave 0.2826 gr. of CO<sub>2</sub> and 0.0506 gr. of H<sub>2</sub>O.

		Calculated for C <sub>6</sub> H <sub>6</sub> I <sub>2</sub> N <sub>2</sub> O <sub>2</sub> .	Found.
C	...	18.46	19.00
H	...	1.02	1.38
I	...	65.12	65.66

Di-iodometanitriline is almost insoluble in water; alcohol, hot or cold, dissolves it with ease. It is but slightly soluble in cold acetic ether. Its melting point is 145½°. The yield is almost the theoretical amount. Concentrated nitric acid dissolves in the cold without decomposition.

By boiling with concentrated chlorhydric acid, di-iodometanitriline is converted into its chlorhydrate. This compound crystallizes in white needles, which are very easily decomposed by water. It also decomposes when heated above 50°. An analysis of the salt, dried in a vacuum, gave the following numbers: 0.1372 gr. of substance gave 0.0475 gr. of AgCl.

	Calculated for $C_6H_4I_2N_2O_2HCl$ .	Found.
Cl	8.30	8.57

The mother-liquors, from which the di-iodometanitriline was recrystallized, yielded, upon dilution with water, a second iodine compound, together with small quantities of the above described body. This compound crystallizes in yellow plates, and differs from the di-iodometanitriline, in that it is very soluble in cold acetic ether and much more soluble in alcohol. A partial separation can be effected by means of acetic ether, but we were unable to obtain the compound in a state of purity. It melts between 85 and 95°, and is probably a moniodometanitriline. The yield of this compound was not increased by acting upon 1 mol. of nitraniline with 1 mol. of iodine chloride.

*Action of Iodine Chloride upon Paranitriline.*

One molecule of nitraniline was dissolved in dilute chlorhydric acid, and treated with 2 mols. of iodine chloride. The liquid was allowed to stand several days, and then diluted with water. A beautiful, yellow, crystalline precipitate gradually separated, which consisted of two compounds. These were separated by extraction with hot water, which dissolved one, while the other remained as a brown crystalline residue. The hot aqueous solution deposited, on cooling, a mass of long, yellow needles, which were easily purified by recrystallization from water. The proximate analysis of the substance, so obtained, gave the following numbers: 0.1559 gr. of substance gave 0.1384 gr. of AgI. 0.3306 gr. of substance gave 0.3360 gr. of  $CO_2$  and 0.0664 gr. of  $H_2O$ .

	Calculated for $C_6H_5IN_2O_2$ .	Found.
C	27.27	27.71
H	1.89	2.22
I	48.10	47.91

Mono-iodoparanitriline is easily soluble in alcohol and also in hot water, only slightly in cold water. It melts at 105½°. The yield is about 75 p. ct. of the theoretical amount. It is a weak base; the chlorhydric acid salt is very easily decomposed by water, and so unstable that no satisfactory analysis could be obtained.

The brown residue, insoluble in water, mentioned above, consists of a second compound, which was purified by several crystallizations from a mixture of alcohol and nitrobenzene. The yield of this substance was so small that we endeavored to obtain a larger quantity by the action of  $\text{ClI}$  on the nitraniline, instead of its chlorhydrate. For this purpose 1 mol. of para-nitraniline was dissolved in chloroform, and treated with 2 mols. of iodine chloride. We obtained in this manner the substance in almost the theoretical quantity. Most of the iodine compound separated from the chloroform upon standing; the remainder was obtained by the addition of alcohol, and the evaporation of the chloroform. The body is best purified by two crystallizations from a mixture of equal parts of alcohol and acetic ether. The analysis was as below: 0.1209 gr. of substance gave 0.1460 gr. of  $\text{AgI}$ . 0.2177 gr. gave 13.5 cc. of  $\text{N}$ . Bar = 745.5;  $t = 3^\circ$

		Calculated for $\text{C}_6\text{H}_4\text{I}_2\text{N}_2\text{O}_2$ .	Found.
I	...	65.12	65.25
N	...	7.18	7.50

Di-iodoparanitraniline crystallizes from alcohol in short, bright yellow prisms, which by reflected light have a beautiful blue color. Its melting point is  $243\frac{1}{2}$ – $244^\circ$ . It is but little soluble in hot alcohol, more in chloroform and acetic ether, very soluble in hot nitrobenzene, from which it crystallizes in plates.

*Action of Iodine Chloride upon Paratoluidine.*

The ease with which iodine chloride acts upon acetanilide led us to suppose that it would have a like action on acetparatoluide, but we found that it had no action upon it. This result is surprising, since bromine and chlorine both act easily on acettoluide, with the formation of bromine and chlorine substitution products.

We next investigated the action of 1 mol. of iodine chloride upon a solution of 1 mol. of paratoluidine in dilute chlorhydric acid. The liquid was allowed to stand several hours, during which time a black precipitate settled. This was removed by filtration; upon further standing, a flocculent, nearly white precipitate was deposited, which was purified by two crystal-

lizations from dilute alcohol, and the analysis was as follows : 0.1147 gr. of substance gave 0.1516 gr. of AgI.

		Calculated for $C_7H_7I_2N$ .	Found.
I	...	70.76	71.47

Di-iodoparatoluidine crystallizes in long, white needles, which often form clusters. It melts at  $124\frac{1}{2}^{\circ}$ . It is insoluble in cold water and but slightly soluble in hot, tolerably in cold and easily in hot alcohol. The filtrate from which the iodine compound separated was neutralized with ammonia and yielded unchanged toluidine.

*Action of Iodine Chloride upon Paraamidobenzoic Acid.*

The acid was dissolved in a large excess of dilute chlorhydric acid, and treated with 2 mols. of iodine chloride. After the treatment the liquid was allowed to stand six hours, and then diluted with a large volume of water. In the course of a day, a white mass, consisting of the iodo derivative of the acid, separated. This was filtered, purified by conversion into the ammonium salt, and decomposition of this salt by chlorhydric acid; this process being repeated several times. The analysis of the substance, thus obtained, was as follows : 0.1588 gr. of substance gave 0.1908 gr. of AgI. 0.3504 gr. of substance gave 0.2820 gr. of  $CO_2$  and 0.0550 gr. of  $H_2O$ .

		Calculated for $C_7H_5O_2NI_2$ .	Found.
C	...	21.59	21.94
H	...	1.29	1.74
I	...	65.29	64.93

Di-iodopara-amidobenzoic acid crystallizes in white plates, which melt above  $300^{\circ}$ . In water, alcohol and acetic acid it is insoluble, very slightly soluble in acetic ether. Nitrobenzene dissolves it more readily. The compound does not combine with acids. It is easily soluble in alkalis, forming the corresponding salts. The potassium and ammonium salts crystallize in long, white needles, and are soluble in water. The silver salt was obtained as a flocculent precipitate by the addition of nitrate of silver to an aqueous solution of the ammonium salt. It is slightly soluble in water and alcohol, and very stable toward light. The analysis gave the following result : 0.2917 gr. of substance gave 0.1384 gr. of AgI.

	Calculated for $C_7H_4O_2NI_2Ag$ .	Found.
Ag	21.99	21.80

The sodium salt is easily obtained, in a state of purity, by dissolving the acid in warm caustic soda; on cooling, the salt separates in long white needles, which are quite insoluble in cold, but tolerably soluble in hot water. The crystals contain 5 mols. of water of crystallization, which they lose by heating at  $160^\circ$ .

The analysis of the salt furnished the following figures: 0.2537 gr. lost at  $160^\circ$  0.0468 gr. of  $H_2O$ .

	Calculated for $C_7H_4NI_2O_2Na + 5H_2O$	Found.
$H_2O$ .	17.94	18.05

0.2069 gr. of the anhydrous salt gave 0.0316 gr. of NaCl.

Na	5.59	6.00
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The barium salt was precipitated from an aqueous solution of the ammonium salt by the addition of barium chloride; the product so obtained was purified by two crystallizations from water. The salt is very little soluble in cold water, more soluble in hot, and crystallizes in colorless needles, containing 4 mols. of water of crystallization.

The analysis gave the following figures: 0.4109 gr. lost at  $140^\circ$  0.0320 gr. of  $H_2O$ .

	Calculated for $(C_7H_4I_2NO_2)_2Ba + 4H_2O$ .	Found.
$H_2O$	7.31	7.78

0.3728 gr. of the anhydrous salt gave 0.0950 gr. of  $BaSO_4$ .

Ba	15.00	14.97
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*Action of Iodine Chloride upon Meta-amidobenzoic Acid.*

The acid was treated, as in the previous case, with 2 mols. of iodine chloride. After standing a few hours, a grey, crystalline mass separated. This product was purified by crystallization, and by conversion into an alkali salt, and decomposition of the salt by chlorhydric acid. The analyses of the substance, so obtained, indicated, that it was a mixture of di- and tri-iodometa-amidobenzoic acids.

Numerous attempts to obtain a separation all failed, owing to the like solubilities of the derivatives and salts of the two acids. The results of the analyses from different preparations were as follows:

Calculated for $C_7H_5O_2NI_2$ .	Calculated for $C_7H_4O_2NI_3$ .	Found.
I ... 65.29	74.41	68.11 67.51 67.33 68.48

The analysis of the silver salt was as follows:

Calculated for $C_7H_4O_2NI_2Ag$ .	Calculated for $C_7H_3O_2NI_3Ag$ .	Found.
Ag ... 21.96	17.4	18.96

Iodine chloride does not act upon acetmeta-amidobenzoic acid.

The results obtained in this investigation show the importance of iodine monochloride as a reagent for the production of aromatic iodo-amines.

We present here a tabular view of the cases in which the action of iodine chloride on aromatic compounds has been investigated, showing its substituting power compared with that of bromine and chlorine under similar circumstances. It will be seen that, while iodine chloride replaces hydrogen by iodine in many cases, yet, on the whole, its strength as a substituting agent is less than that of bromine or chlorine.

	Iodine Chloride.	Bromine.	Chlorine.
Acetanilide	mono	mono-di-tri	mono-di-tri
Salts of Aniline	mono-di-tri	mono-di-tri	mono-di-tri
Metanitriline	di-mono (?)	tri	
Paranitriline	mono-di	di	di
Acetparatoluide	no action	mono	mono
Salts of Toluidine	di	mono-di	mono-di
Para-amidobenzoic Acid	di	di	
Meta-amidobenzoic Acid	di-tri (?)	tri	
Phenol	mono-tri	mono-di-tri	mono-di-tri
Resorcin	tri	tri-penta	
Orcin	tri	mono-tri-penta	tri-penta

The determination of the position of the iodine atoms in the above described compounds will require a separate re-

search. The weak basic properties of di-iodoaniline, and the absence of basic properties in tri-iodoaniline, indicate that the second and third iodine atoms entering the molecules have taken the ortho position toward the amido group, since among the numerous known di- and trichloro- and bromoanilines, only those, whose halogen atoms are in the ortho position toward the amido group, show a like loss of basic properties.

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## THE ACTION OF PHTHALIC ANHYDRIDE ON NAPHTHALENE IN THE PRESENCE OF CHLORIDE OF ALUMINIUM.

BY EMILE ADOR AND JAMES M. CRAFTS.

Friedel has shown in a research \* made with one of us, that the action of phthalic anhydride on benzene in the presence of chloride of aluminium is expressed by the equation :



The product, benzoylorthobenzoic acid, is obtained quite pure, and almost in the quantity required by the above equation, when a considerable excess of benzene is taken. If a similar acid could be obtained from naphthalene in equal abundance, the study of its reactions, and particularly of the hydrocarbons to be derived from it, would present considerable interest, and it is from this point of view that we have taken up this subject.

500 gr. naphthalene were heated with 200 gr. pure phthalic anhydride to 100°, and 250 gr. anhydrous chloride of aluminium were gradually added so as to provoke a nearly continuous disengagement of chlorhydric acid. At the end of six hours the product was boiled with water in order to decompose the anhydrous chloride of aluminium. About 50 gr. phthalic acid

\* Comptes rendus, 3 Juin, 1878.

were regained by evaporating the aqueous solution. The principal product was a black tarry mass, which was repeatedly digested with a weak solution of caustic soda. This treatment extracted phthalic acid, besides a small quantity of a less soluble acid, which was the body sought. The purification is difficult, and the method which succeeds the best is to bring it to a certain stage of purity by repeated fractional precipitations by an acid from the sodic solution, then to crystallize 8 to 10 times by cooling from a hot solution of benzene or toluene, and finally to crystallize from alcohol until well formed crystals are obtained. Less than 2 gr. of pure acid were thus obtained.

The analysis gave: Subst. = 0.2415 gr.;  $\text{CO}_2$  = 0.6890 gr.;  $\text{H}_2\text{O}$  = 0.0980 gr.

		Found.	Calculated for $\text{C}_{15}\text{H}_{12}\text{O}_5$ .
C	...	77.85	78.27
H	...	4.51	4.37

The analysis was made after drying the acid at  $130^\circ$ . It appears to contain water of crystallization, but its percentage was not determined. The melting point in a capillary tube was taken of various portions of dried acid, and was always found to be  $173.5^\circ$  (without correction), notwithstanding differences of form according to the mode of crystallization, and the same is true of the first and last portions in a fractional crystallization of the purified acid.

*Naphtoylorthobenzoic acid* crystallizes from hot absolute alcohol on cooling, in rosettes of microscopic prisms, which appear to have a single terminal face, whose edge is at right angles with the axis of the prism; the mother liquor after cooling deposits single prisms with two oblique terminal faces at either end. From a mixture of equal parts of alcohol and water it crystallizes in little stout prisms like those of phthalic acid.

It is insoluble in water, easily soluble in alcohol, less soluble in cold benzene or toluene; from these latter it crystallizes in indistinct forms. The acid decomposes on distillation.

The barium salt was formed by adding baryta water to an alcoholic solution of the acid and precipitating the excess of baryta by carbonic acid, and crystallizing the salt from its aqueous solution. The analysis of the dried substance gave 20.95 per cent. Ba instead of 19.94, and it is probable that

some basic salt was present, because the solution deposited during the evaporation a crystalline crust which was difficultly soluble in water. We had too little substance to complete the purification or determine the water of crystallization. The crystals dried over sulphuric acid are very hygroscopic, and lose 2.7 per cent. more water on drying at  $150^{\circ}$ ; at about  $160^{\circ}$  the salt becomes vitreous, and melts at a higher temperature before decomposing.

The *barium* salt crystallizes by evaporation of the aqueous solution in microscopic needles. It is pretty soluble in water and even in alcohol.

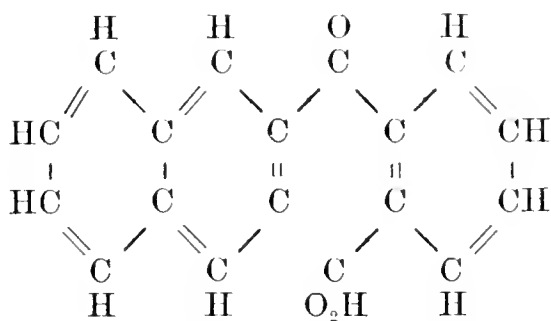
It will be seen by the foregoing statements that the reaction which gives rise to the naphthoylorthobenzoic acid is not a simple one, and that it cannot be prepared in considerable quantity by this method, nor did some other attempts at preparation give more favorable results. It remains to examine the accessory products. The uncrystalline matter which is furnished by the first fractional precipitations of the sodium salt of the acid, as well as the product insoluble in soda after extraction of the naphthalene by boiling alcohol, are very difficult to purify. The latter is the principal product formed in the reaction, and probably contains a certain quantity of naphthoylbenzoic acid. It is a black mass, which is decomposed in great part on distillation at a temperature higher than  $300^{\circ}$  with formation of a little water. The distillate is a viscous liquid, which, dissolved in benzene, gives on addition of alcohol a small quantity of crystalline flakes. These crystallize from a mixture of ether and alcohol in a granular form. The melting point is  $181^{\circ}$ – $186^{\circ}$ . The crystals cannot be sublimed and appear to suffer partial decomposition on distillation. An analysis gave:

		Found	Pyrene.	Chrysene.
C	...	94.18	94.12	94.73
H	...	5.89	5.88	5.27

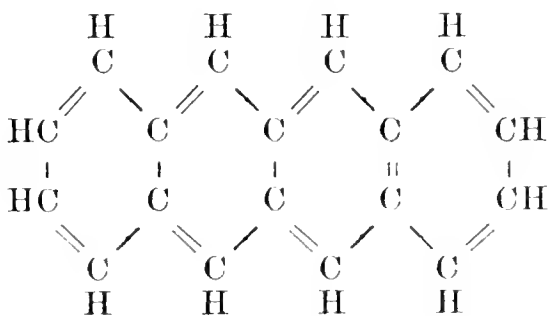
Although the empirical composition is like that of pyrene or chrysene, the properties of this hydrocarbon are very different. It forms no combination with picric acid, and dilute or concentrated nitric acid does not oxidize it, but gives a resinous nitrated product soluble in alcohol. The solution in bisulphide

of carbon treated with bromine forms a substitution product little soluble in alcohol, easily soluble in ether. It crystallizes in granular form and melts at  $112^{\circ}$ .

Only one-half gram of the hydrocarbon was obtained, and it must be regarded as an accessory product, so that any theory of its composition which implies its derivation from known bodies by a smooth reaction is entitled to little weight. The following hypothesis, however, may be worthy of notice: From the well-known stability of the hydrocarbon groups entering into the reaction we may suppose the new hydrocarbon to contain the 10 atoms of carbon of naphthalene plus the 8 atoms of phthalic anhydride, and in that case it would be an isomere of chrysene,  $C_{18}H_{12}$ . It may be derived from naphthoylorthobenzoic acid,



by the closing of the chain and the loss of 3 atoms of oxygen,



This view of the internal structure of the new hydrocarbon is interesting, as it represents it as composed of two molecules of naphthalene having two carbon atoms in common.

## NOTE ON PARA-NITRO AND PARA-AMIDO PHENETOL.

BY E. J. HALLOCK.

Phenetol is violently attacked by fuming nitric acid, but is unaffected by concentrated nitric acid in the cold. Cahours, who first tried the action of fuming nitric acid upon phenetol, obtained, he says,\* both a solid and liquid product. The former he analyzed and found it to be dinitrophenetol; the latter he supposed to be mononitrophenetol. The writer repeated these experiments with somewhat different results. The dark-red viscous liquid obtained by the action of fuming nitric acid upon pure phenetol, or on a solution of phenetol in acetic acid, was distilled in a current of steam. The product consisted of a solid and a liquid, in varying proportions according to the conditions of the nitration. The solid, when purified by repeated recrystallization both from acid and from alcohol, was proved by an ultimate analysis to be a mononitrophenetol.† Its melting point, 58° C., and other physical properties coincided with that of para-mononitrophenetol, prepared by Fritzsche in 1858 by the action of iodide of ethyl upon the silver salt of paranitrophenol.‡ The writer also obtained the same body by the action of potassium ethylic sulphate and potassic hydrate upon paranitrophenol in sealed tubes at high temperatures. In this operation, however, a considerable quantity of the nitrophenol remained unchanged. Iodide of ethyl and potassic hydrate heated in a sealed tube with paranitrophenetol also yielded, as was expected, the same body, but quite impure. The method of direct nitration yields the purest product, but is quite tedious. When the nitration was performed with nitric acid from which the red fumes had been removed by previously boiling, or by means of hot concentrated acid, the product is mostly liquid

\* Ann. Ch. Phys. [3] 27, 461.

† The analysis gave

		Found.	Theory.
C	...	57.3	57.5
H	...	5.9	5.4
N	...	6.0	8.4

‡ Petersb. Acad. Bull. 17, 145; Ann. der Chemie, 110, 155.

and refused to crystallize, even at low temperature. This liquid was apparently a mixture of orthonitrophenetol and unchanged phenetol, holding some paranitrophenetol in solution.

Having obtained a considerable quantity of the paranitrophenetol, an attempt was made to reduce it by means of tin and hydrochloric acid. The resulting salt, after the removal of the tin with sulphydric acid, crystallized from water, in which it was very soluble, in rhombic plates with a pearly lustre. An ultimate analysis\* established the composition as  $\text{HCl}, \text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{NH}_2 \end{smallmatrix}$ . With platinum chloride it yielded a very beautiful double salt in bright golden flakes, but easily decomposable, especially when heated.

These crystals, when treated with potassic hydrate, yield an oily liquid resembling aniline. It boils at  $253^\circ \text{C}$ . (uncorrected), and is doubtless *paramonamidophenetol*. A portion of the salt appears to suffer a farther decomposition, so that the amount of oil obtained was very small. This oil combines, like aniline, directly with acetyl chloride to a crystalline solid. In combination with carbon disulphide it also yields a solid body. The writer did not succeed in obtaining this amidophenetol by the action of ammoniac sulphide upon the nitrophenetol at high or low temperature.

The black mass remaining in the flask, after the mononitrophenetol has been distilled off, contains dinitrophenetol, but is difficult to purify.

\* The analysis gave

		Found.	Theory.
C	...	55.6	55.4
H	...	7.4	6.9
N	...	8.9	8.1
Cl	...	20.6	20.4

## REVIEWS AND REPORTS.

## BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

*(Continued from page 203.)**Heavy Chemical Manufactures—Acids, Alkalies, and Materials immediately connected therewith.*

*Sulphur.*—By far the largest supplies of native sulphur still come from Sicily, although recent surveys of the volcanic region from whence these supplies are drawn render it improbable that the approach to monopoly which the island has long enjoyed can for many years, say for half a century, be maintained. Of late years the Romagna has added a respectable quota to the Italian supply, and several smaller deposits, as in Galicia, Spain and Egypt, have been worked; but the great field presented in Iceland, of which highly favorable reports have been made, and which has recently, and more than once in the past, been entered upon, has not yet been made practically important. For the future chemical industry of the United States, the deposits at present known which are likely to become of great value are those of Nevada and the adjoining portions of California, the remarkable bed pierced by borings in Western Louisiana but still unworked, and perhaps the volcanic products of Hawaii and the Chilian Andes.

As regards the method of extraction of native sulphur from the gypsum and other earthy materials with which it is found associated, the simple process of piling up the "sulphur stone" in large heaps, arranged very much like those in which charcoal is burned, and melting out part of the sulphur by the heat produced in the smothered combustion of the remainder, is almost exclusively resorted to, and the scarcity of fuel in Southern Italy will probably always cause it to be there retained, in spite of the great loss of sulphur, of which at the best one-third is commonly destroyed or not made available in obtaining the remaining two-thirds. Attempts at less wasteful modes of treatment, as fusion in close vessels by means of high pressure steam, or solution by means of carbon di-sulphide, have made but little progress in the chief regions of production, mainly in consequence of the cost of fuel; the latter process, that by solution, is said to give very satisfactory results in Austrian Galicia. A simple observation made a few

years ago by Sestini,\* to the effect that somewhat above 400° C. calcium sulphate and sulphur react upon each other with evolution of sulphur dioxide,



indicates the importance, in the ordinary process, of keeping down the temperature of the heaps of sulphur stone, and this may perhaps serve to diminish the loss in the usual practice. The same precaution is indicated, however, with even greater urgency by recollection of the fact that at a temperature but little above its fusing point melted sulphur begins to thicken, its viscosity soon increasing so much as to greatly impede its draining away from the earthy impurities.

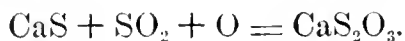
The consumption of sulphur, tending to rapid increase from the ever-growing manufacture of sulphuric acid, the extensive application of late years of sulphur and sulphur compounds to the prevention of grape disease in the vineyards of Europe, and other causes, has been largely economized by the introduction, in workable form and on no small scale, of processes for the artificial making or regeneration of sulphur from the "alkali waste" (calcium sulphide) of the soda manufacture. Of these processes those devised by Mond and Schaffner may be considered typical, both involving partial oxidation of the alkali waste by exposure to air containing carbon dioxide, under regulated conditions of temperature and amounts of air and water, thus producing thio-sulphate and poly-sulphides of calcium, followed by precipitation of sulphur from the mixed solution by hydrochloric acid, calcium chloride being the chief by-product. The final reaction under Mond's treatment seems to be mainly



while Schaffner aims at the result



the  $\text{SO}_2$  being passed into fresh alkali waste lye in order to convert more calcium sulphide into thio-sulphate,



Other reactions, however, appear to take place to some extent under varying conditions, and it is desirable that in alkali works employing these processes for sulphur regeneration careful account should be kept of the yield actually obtained, and that this should be checked by frequent assays of the material used.

\* Bull. de la Soc. Chim. de Paris, 24, (1875), p. 490.

To a very limited, scarcely more than experimental, extent sulphur has also been recovered from the Laming mixture for purifying coal-gas,\* essentially ferric hydrate, which, after use in removing sulphur from the gas, may by exposure to the atmosphere be restored to its original condition, with separation of free sulphur, which may be accumulated by repetition of the same steps. Much the greater part, however, of the coal used in making illuminating gas, and practically all that employed as fuel, is so treated as to involve the loss of the whole of the sulphur it contains. For the world at large it is not an excessive estimate to set down this as equal to one per cent. on 270,000,000 tons of coal annually, or 2,700,000 tons — more than seven times the whole sulphur product at present. To this must be added a very large loss from the roasting of sulphurous metallic ores without utilization of the sulphur driven off. The production of sulphur as such from pyrites makes but little progress, and must be viewed as of very secondary importance, but the indirect economy resulting from the large scale on which pyrites is now used for making sulphuric acid is of the greatest value, and has served to prevent scarcity and rise of price of sulphur itself being, before now, sharply felt. The problem of the cheap and practically successful production of sulphur from gypsum remains in abeyance, and seems likely to remain so until the market conditions as to other sources of supply undergo notable change.

No remarkable departure has for some time been made from the established practice of sulphur refining, save that a few years ago the extensive use of flowers of sulphur in combating vine disease led to such regulation of the temperature of the distilling chambers as enabled a larger share than before of the product to be collected in this, the sublimed form.

### *Acids.*

*Sulphuric Acid.* — The scale upon which this fundamental reagent of the manufacturing chemist is made continues to increase, and there is observable an increasing tendency to connect its production with other industries, so as to secure, when not otherwise attainable, a saving of the heavy charges for transportation of so destructive a material.

It is but forty years since the first decided inducement to substitute pyrites for native sulphur in this manufacture was given by the threatened scarcity of the latter, due to the grant of a monopoly of Sicilian sulphur to a Marseilles house; but within this time, and especially the last few years, the extension of the use of pyrites has been so great that now seven or eight tons of acid are probably made from it for one made from free

\* Sulphur from this source is more readily utilized in the manufacture of sulphuric acid.

sulphur. This change has been partly aided by notable improvements in the kilns for burning pyrites, but largely also by the economy effected by metallurgic treatment of the burnt residue. Beginning with the saving of copper from cupriferous pyrites (like that so abundantly found in Spain and Portugal), too poor in this metal to be treated solely as one of its ores, by methods which have already been alluded to in this paper, means have since been found for obtaining also the relatively very minute quantities of silver and gold often found present, and still more recently the burning off of sulphur in the kilns has been so far improved that the residue of ferric oxide may be smelted into pig iron of very fair quality. Beside pyrites, the sulphides of lead, zinc and other metals, and the sulphur of Laming's mixture from coal gas works, have been used, but to a very limited extent only.

As regards the mode of preparing and introducing into the apparatus the nitric acid vapor needed in the production of sulphuric acid, English and Continental practice differ in Europe; in France and Germany, liquid nitric acid, prepared by a separate distillation, is preferred, with a suitable drip contrivance for regulating its flow, while in England "nitre pots" are in general use, heated by the gaseous current from the sulphur or pyrites burners, and adding to this current directly nitric acid vapor. It may seem worth considering whether such addition in the state of vapor might not better be made from small external stills of iron or stoneware, delivering their product into the rear part of the sulphur burner or into the flue leading therefrom, but heated separately, perhaps by steam jacketing of suitable temperature, and thus admitting of independent regulation of temperature.

With a view to determining the best shape and size for the leaden chambers, about which there is still much difference of opinion, it is greatly to be desired that systematic observations, and as far as opportunity may offer experiments, be made upon the scale of actual practice. In the working of the chambers, probably the most valuable novelty has been the introduction by Sprengel, instead of jets of steam, of cold water injected as spray by the aid of a little steam, thus enabling the supply of the necessary amount of water to be combined with the nice regulation of temperature.

Great interest attaches to the comparatively new "Glover tower" which is replacing the old form of de-nitrating tower of Gay Lussac's well-known contrivance for saving nitrous gases. In the original arrangement, the current of gases from the pyrites kilns often required to be cooled before reaching the leaden chambers or the de-nitrating tower, while in the latter the nitrous gases were liberated from the strong acid, brought from the absorbing tower, by means of steam or hot water, thus diluting this acid so far as to unfit it for imme-

diate use again as absorbent. In the upper part of the Glover tower, weak acid from the leaden chambers and strong nitrated acid are allowed to mix, thus liberating the nitrous gases, while in the lower part of the same tower the acid encounters the hot gases from the pyrites kilns, and the transfer of heat from the latter to the former accomplishes the double purpose of cooling suitably the gases and concentrating the acid to such a strength that it can be used over again in the absorbing tower or utilized as part of the final product.

In the transfer of acid from place to place in the works improvements have been effected in the pumps, partly of stoneware capable of resisting the action of the acid, partly bringing to bear compressed air, so that the working parts need not be exposed to contact with the corrosive liquid. Not only in this relation, but in a multitude of chemical processes upon the large scale, the command of hard stoneware, cheap and withstanding well both high temperatures and energetic chemical reagents, is an advantage of the present day comparable with the improved glass and porcelain which our laboratories of research are so well provided with.

The least satisfactory feature of the great manufacture in question is perhaps the amount of nitre still consumed, although this has been much reduced since the days that preceded Gay Lussac's improvements. The chief causes of the loss experienced are doubtless —

1. Gaseous compounds of nitrogen escaping at the final outlet or chimney, where theoretically nothing but atmospheric nitrogen in the free state should find exit, and this in spite of the use of a Gay Lussac's absorbing tower.

2. Nitrous compounds carried off in solution in the liquid acid made, this form of loss probably leading also to increased rate of destruction of the platinum stills for concentration, the metal of which is now known to be slowly but surely dissolved, apparently even by pure sulphuric acid.

3. Reduction of the other oxides or acids of nitrogen to the monoxide or even to elementary nitrogen, both incapable of performing the function of again taking up oxygen from the air. Such reduction, favored by too high a temperature, but liable to occur under conditions not yet, it would seem, fully understood, may take place in the leaden chambers, in the de-nitrating tower, or in the connecting flues back to the nitre pots.

From the careful investigation of this question of nitre consumption, immediately practical results, in the shape of reduced cost of acid production, may be looked for. We are still far from able to make oxygen on a sufficiently great scale, and at a low enough price, to admit of the pure gas being substituted for common air in the chambers, which might in that case be made closed, but it may be well to

avoid laying aside this suggestion, long ago made, as involving a permanently impracticable idea.

For the concentration of the acid to full strength, although glass vessels are not out of use, those of platinum are of most importance, and in the form and arrangement of the latter sundry improvements have been devised, especially by the intelligent firm of Johnson, Matthey & Co. of London. Economy of platinum is secured to a valuable extent by the open pans of the precious metal, with capitals or hoods, connecting tubes, &c., of lead, which have recently been introduced in improved form by Faure and Kessler of Clermont-Ferrand.

In connection with the manufacture of sulphuric acid may be noticed with interest the quite recent production on an industrial scale and presentation in the market of sulphur trioxide or so-called anhydrous sulphuric acid, which replaces with advantage both the ordinary oil of vitriol and the Nordhausen or fuming acid for certain purposes, such as the production of the sulpho-acid-derivatives of benzene, toluene, anthracene, &c., employed in the manufacture of chemical dye-stuffs. The trioxide is obtained by dripping common sulphuric acid into red-hot retorts, thus breaking it up into water, oxygen and sulphur dioxide, condensing the first of these, and causing the two latter to unite by passing them over platinized asbestos or similar porous material at a proper temperature. Both the solid trioxide, retaining but traces of the acid, and an oily, liquid, fuming sulphuric acid, holding 80 or 90 per cent. of trioxide, can now be had at very reasonable prices.

*Nitric Acid.*—There is little to note with reference to the production of this acid, except that sodium nitrate from Chili may be said to have for some years past become the universally employed material, and horizontal cast-iron cylinders the apparatus generally used for the distillation. Slight modifications in detail of the condensing vessels are made from time to time.

*Hydrochloric Acid.*—This has long been essentially a secondary product of the alkali manufacture as conducted by the method of Leblanc, but the condensation of the acid has been much improved of late years, the first strong impulse in this direction having been given by the English "Alkali Act" of 1863, directed against the nuisance arising from destruction of vegetation by the acid gas when allowed to escape from the soda works. Since then increased supply of the liquid has conspired with increasing extent and variety of demand for it to still further improve the condensation, and like pains have been bestowed upon the same object in France and Germany. Sandstone or stoneware vessels for the strong acid, and coke towers for the weaker after-products, constitute the apparatus used. A problem already of much importance and promising to become more important in the near future, is presented in

the idea of making, by a cheap and simple process, hydrochloric acid (or chlorine) from the *calcium* and *magnesium* chlorides. The former of these is even now turned out as a waste product of several chemical industries on a very large scale, and from the extension of the ammonia-soda process and other sources vast additional quantities may hereafter be looked for. The latter—magnesium chloride—is available in large amount as a by-product of the treatment of the Stassfurt potash deposits. Solvay's recent proposal to treat these chlorides with silica or alumina can hardly be looked upon as a satisfactory solution of the problem, the temperature required being probably too high for economical results, and the utilization of the solid residues very doubtful.

*Acetic Acid.*—The two methods by which this acid is made—oxidation of alcohol and destructive distillation of woody fibre—remain without material change, the extent of the manufacture in both directions having, however, grown largely, mainly with the growth of dyeing and calico-printing. The elaborate researches of Pasteur and others upon the phenomena of fermentation have had some little practical application to the work of the vinegar-maker in directing the artificial *sowing* of the ferment organism, and in regulating the conditions for rapid and effectual conversion of the alcohol. The great extension of refined processes of organic chemistry, chiefly among manufacturers of the newer dyes, has produced a demand in the general market for "glacial" acetic acid, which is now made upon a pretty large scale, while but a few years ago it belonged solely to the domain of the scientific and pharmaceutical laboratory.

*Oxalic Acid.*—Dale's beautiful process for making this product from saw-dust by heating with an alkaline hydrate has displaced all other methods. Founded on experiments of Gay Lussac made half a century ago, the process was first given practically useful shape by Dale in 1856, was for a number of years altogether an English industry, but has of late been adopted also on the Continent of Europe. In Germany caustic potash alone is said to be used, but Dale's own method of working with a mixture of potash and soda (the latter by itself will not answer the purpose) seems distinctly the more advantageous, as allowing of the difficultly soluble sodium oxalate being in large measure purified by washing before it is decomposed by lime. An improvement is said to have been effected by washing the saw-dust beforehand with a weak alkaline solution, thus removing incrusting matter and affording a nearer approach to pure cellulose to be fused with the potassium and sodium hydrates. Great increase of production and lowering of price have followed the successful working of Dale's patent.

*Alkalies (Carbonates and Hydrates).*

*Potash.*—Within the last twenty years the production of this alkali has undergone a complete revolution. The crude potash from leaching wood ashes, which formerly represented nearly the whole of the world's supply, has come in much diminished quantity from the forests of Russia, Canada and the Northern United States, and has almost ceased to appear from several of the smaller regions of production—it now forms less than 40 per cent. of the general stock in market. Its place has been largely taken by a purer carbonate made, by Leblanc's classical process, from the sulphate of the newly discovered Stassfurt beds, and by like material derived from the ashes of beet-root molasses, and from the wash water used in cleansing sheep's wool.

In the manufacture of the first of these newer products there have been numerous, and in large measure successful attempts to prepare the sulphate of potassium by crystallizing mixed solutions of the crude potassium chloride (carnallite) and magnesium sulphate (kieserite) found together in the great treasure-house of saline material found overlying the rock salt of the Stassfurt region, but on the whole it seems to have proved more economical to act with sulphuric acid on potassium chloride purified by previous crystallizations and washings, and thus to carry on the whole process as in the common soda manufacture. It is to this method that we must in all probability chiefly look to meet the future increase of demand for potash.

The second method, calcination of the residue from the stills in which the alcohol of beet-root molasses has been driven off, has gained in importance of late years with the rapid increase of production of beet sugar, but the tendency now is, and most likely in the future will be, rather in the opposite direction, more of the crude residues being directly utilized as manure upon the beet crop itself, instead of, as formerly, being worked up into potash for sale. There have been one or two modifications of the method of treatment introduced of late, as the use by Camichel and Henriot of tanner's chestnut extract instead of sulphuric acid to acidify the diluted molasses in preparing it for fermentation, thus obtaining more potassium carbonate and less sulphate after calcination, and the system of C. Vincent of submitting the evaporated still residue to destructive distillation in closed retorts, with a view to utilizing the volatile products (ammonia, trimethylamine, &c.), instead of burning off the organic matter in open hearths.

The third of the newer sources of potash, the "suint" left on evaporation of wash-water from wool factories, has also been employed in both ways, by distillation in retorts, utiliz-

ing the gaseous products for the illumination of the factories (original plan of Maumené and Rogelet), and by calcination in the air. The process seems to have yielded fairly profitable results, but has not established itself on such a scale as to utilize nearly all the washings of even the European wool manufacture. Its general importance is much less than that of the preceding methods.

*Soda*.—The recent history of the soda manufacture involves notice of improvement in the Leblanc process and of other methods which have been to some extent substituted for it.

1. *Modifications of the Leblanc Process*.—The first step as commonly carried out, decomposition of common salt by sulphuric acid, has been facilitated by the modern use of improved forms of the salt-cake furnace, while no small success has attended the plan proposed by Hargreaves for avoiding the cost of making and using sulphuric acid, by passing a gaseous mixture of sulphur dioxide (from pyrites burners), steam and air through a porous mass of salt heated in a special furnace to a temperature a little below redness. The soundness of the principle on which this method is based was long ago established, and of late the mechanical and other difficulties in detail of application have been so far overcome that salt-cake is regularly made in this way on the large scale by a number of factories in England.

The second stage of the process, fusion of the sodium sulphate with coal and chalk, has been made to profit by two of the prominent features of improved furnace construction, the mechanical "black-ball furnace" being heated by gaseous fuel on the Siemens principle and furnished with a revolving hearth, which enables the hand-working of the contents to be dispensed with and excludes objectionable admission of air. Fuel is economized by the employment of "regenerator" chambers and final use of the waste heat from the escaping gases to evaporate soda liquors from previous operations. At this stage of the chemical treatment Mactear's simple improvement may be noticed, consisting in keeping down the quantity of chalk to the strict demands of theory, and throwing into the hearth, after the reaction is over and just before drawing the charge, a small amount of quick-lime, to be rapidly mixed with the mass by revolving the hearth again for a short time, this last addition serving the purpose, as an excess of calcium carbonate introduced at first had formerly but less advantageously done, of slaking on exposure to moisture, so as to disintegrate the lumps of black-ball and fit them for rapid and effectual leaching.

There has been no recent change of first-rate importance in the process of leaching, nor in the subsequent evaporation of the liquors and purification of the alkali; but the successful utilization of the insoluble residue of the leaching, the "tank

waste," chiefly, as above noticed, for the recovery of sulphur, and to a subordinate extent for the production of sodium thio-sulphate and other purposes for which calcium sulphide may be used, has at the same time reduced the cost of alkali manufacture, and greatly mitigated, if not removed, a long complained of source of nuisance and inconvenience.

2. *Substitutes for the Leblanc Process.*—Of these, in the shape of experiments and patented projects, there have been very many, but only two have established themselves in practical form.

The ammonia-soda process, originally proposed some forty years ago, has but very lately been put into successful working shape by M. Solvay of Brussels. Starting with the same material as that of the Leblanc process, namely common salt, it treats it by an entirely different method, consisting essentially in absorbing gaseous ammonia by strong brine, passing in carbon dioxide under a pressure of about two atmospheres, preventing rise of temperature by special cooling arrangements, and so obtaining a deposit of difficultly soluble acid carbonate of sodium. This is separated, washed and heated to produce the neutral carbonate, while the residual solution, holding ammonium chloride, is heated with lime to drive off ammonia as gas, which is employed in a repetition of the process. The carbon dioxide is obtained by lime-burning with the aid of jets of steam. The intrinsic value of this method and the possibility of its completely replacing that of Leblanc have been much discussed. The latter is still in use for the production of much the larger part of the soda manufactured, while the newer process has proved its capability of at least competing therewith in the markets of the world, and is being extended to new factories, particularly in France.

The chief advantages of the ammonia process may be briefly stated as—

- a. Great purity of product.
- b. Diminished consumption of fuel.
- c. Absence of all noxious escape of gases, either during the manufacture itself or from the waste products.
- d. Reduction of loss from, at best imperfectly recovered, valuable material consumed (sulphuric acid of Leblanc process).
- e. Possibility of utilizing salt in the form of strong brines, without requiring boiling down to solid salt.

The chief drawbacks of the process are the following:

- a. Failure to make the chlorine of the salt available for industrial purposes, this assuming the, at present, useless form of calcium chloride. As has been above noticed, it would be of itself a most important achievement to devise a really workable method of making from this material hydrochloric acid, and hence chlorine and its various derivatives. Such a method would vastly increase the chances of the ammonia process becoming *the* process for the manufacture of soda.

*b.* Sensible loss of ammonia—although theoretically the same ammonia may be used over and over again indefinitely, and although the loss in practice has been much reduced, it is still not inconsiderable, and hence the process is to a certain extent dependent upon the cost of ammonia, and the effect upon it of varying demand and supply. Improvement in this direction is possible and much to be desired.

*c.* Imperfect conversion into carbonate of the sodium chloride used. Quite a large part of the salt remains as such mixed with the calcium chloride in the waste residual liquor.

In any discussion of the relative merits of the two systems, the complicated and intricate relations of the by-products to other branches of chemical industry must not be overlooked. In proposing to replace a Leblanc factory by one working the ammonia-soda process, not only has the immediate cost of discarding old "plant" and substituting for it new to be faced, but also the complex and far-reaching commercial disturbance due to breaking up a system of combined manufacture of hydrochloric acid, bleaching powder, chlorate of potash, sulphuric acid, copper saving, &c.

The other partially successful substitute for the Leblanc process, namely the production from cryolite of carbonate of soda, with alum, copperas, &c., as by-products, decomposing the cryolite in the first instance by treatment with lime at a low red heat, leaching the mass with water, precipitating the clear liquor with a stream of carbon dioxide, and evaporating the solution thus freed from aluminum as hydrate, has been worked for some years at Copenhagen, in Denmark, and Natrona, Pennsylvania. It furnishes soda of excellent quality, but the limited supply of cryolite, drawn from a single locality on the ice-bound coast of Greenland, must of itself continue to render the method one of merely subsidiary importance.

A change in the alkali manufacture which should not be left unnoticed is the production no longer of all the soda turned out, or nearly all, in the form of carbonate, a very large amount of the hydrate being now, and for a number of years past, also manufactured, chiefly for soap-boilers' use. Instead, moreover, of rendering caustic the finished carbonate, the crude liquors left after a single crystallization are worked up into caustic soda, which thus becomes an independent product of the factory.

*Ammonia.*—For several years past there has been large increase of demand not only for ammonium sulphate, but for caustic ammonia, growing out of the extending use of Carré's ice-machines, the advance in refined chemical manufactures, as of organic dye-stuffs, &c., and lately the introduction of the ammonia process for soda manufacture.

The staple, almost the only material used for obtaining ammonia is still gas liquor, and the method of treating it has

not recently undergone any very great change. Direct saturation of the liquor by an acid was long since given up, and distillation of the crude liquor, to which lime is added, usually by means of high-pressure steam, with or without the aid of air blown through the liquid, is practically always resorted to, the ammonia driven out being condensed in acid contained in a separate vessel, and for the most part so manufactured into sulphate; while for the production of caustic ammonia the gas, derived either from decomposition of a previously prepared ammoniacal salt or directly from the crude ammoniacal liquor, is carried into water in condensers presenting adequate surface. There have been a number of improvements in the details of the distilling and condensing apparatus, of which the most noteworthy involve the principle of so-called dephlegmation. A good example may be found in Solvay's recently invented form of apparatus for concentrating the ammoniacal liquor of the gas works.

Dr. Frank has not long since suggested the desirability of saving both the ammonia and the tar, which are at present lost upon a very large scale in the working of coke-ovens; but, while admitting the magnitude of the loss now suffered and the importance of finding means for preventing it, the fact should not be overlooked that in all the processes of destructive distillation carried out on the large scale it has been found very difficult to secure the best results at the same time as to the fixed and the volatile products, preserving meanwhile reasonable economy as to the form of apparatus, simplicity in the method, and amount of labor and time consumed.

The great problem of making ammonia synthetically from atmospheric nitrogen remains apparently as far as ever from an industrially available solution, but numerous attempts at such continue to appear in the form of an annually increasing number of patents.

J. W. MALLET.

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#### REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

*Hydrogen*.—According to J. W. Thomas,\* when hydrogen, or any other combustible gas, is mixed with oxygen, and the pressure reduced to 160-170 mm., a complete combustion may be effected by means of the spark, without danger to the eudiometer. The tubes employed may be much shorter than those required when dilution is depended upon to diminish the force of the explosion. To separate hydrogen from marsh gas and nitrogen, W. Hempel† employs with success partially oxidized palladium.

\* Jour. Chem. Soc. 1879, 213.

† Berichte d. d. chem. Gesellschaft, 12, 636.

From numerous careful experiments on the occlusion of hydrogen by copper, G. S. Johnson\* concludes, that it is unsafe to employ the freshly reduced metal in organic analysis, unless it has been previously ignited in a current of nitrogen.

*Oxygen.*—O. Lindemann† describes an apparatus employed by him for the estimation of free oxygen in the gases of the sulphuric acid chamber by means of wet phosphorus. Mawson and Swan‡ also describe an apparatus for the determination of free oxygen.

G. Huefner§ has published an article on the determination of oxygen and hemoglobine in blood, by means of the spectrophotometric method.

*Water.*—C. M. Tidy|| discusses the several methods employed to estimate the organic matter in potable waters. He asserts that the combustion method of Frankland, and the oxidation method by permanganate of potassium, give closely concordant results, while the results of the ammonia process of Wanklyn are often at direct variance with both. He considers the oxidation method more reliable than any other.

G. Lechartier¶ has ascertained that there may be a loss of nitrogen in the Frankland process from both nitrates and ammonium salts during evaporation, the sulphurous acid reducing the former, and the carbonates decomposing the latter. He has furnished new proofs, that when a solution containing salts of ammonium and nitrogenous organic matter is evaporated with magnesia, the ammonia of the former may be completely eliminated without decomposing the latter. He proposes, therefore, to give up the attempt to determine simultaneously the organic carbon and total nitrogen in potable waters; and, instead, to determine 1. the nitrogen remaining after the removal of the ammonia by means of magnesia; 2. the nitrogen contained in the nitrates; 3. the carbon independently.

To determine very minute quantities of carbon in waters and elsewhere, A. Dupré and H. W. Hake\*\* propose two methods. The first consists in conducting the carbonic anhydride obtained by burning the residue in oxygen, into a solution of barium hydroxide, and estimating the precipitated barium as sulphate. The second, called by them nephelometric, consists in conducting the carbonic anhydride into a weak solution of basic acetate of lead, and comparing the turbidity produced with that of standards previously prepared.

Other articles of some interest pertaining to water analysis have appeared under the following titles: "Examination of Water for Bacteria," by C. Himly;†† "On Water Analysis," by E. Bohlig;‡‡ "Investigation of the Mineral Water at Ros-

\* Jour. Chem. Soc. 1879, 232.

† Chem. News, 39, 132.

‡ Jour. Chem. Soc. 1879, 46.

\*\* Jour. Chem. Soc. 1879, 159.

† Zeitsch. anal. Chemie, 18, 158.

§ Zeitsch. physiolog. Chemie, 3, 1.

¶ Comptes rendus, 89, 231.

‡‡ Zeitsch. anal. Chemie, 18, 117.

‡‡ Zeitsch. anal. Chemie, 18, 195.

heim," by F. B. Power;\* "On the Air contained in Sea Water," by H. Tornoë.† H. Geissler‡ has invented and patented an apparatus for the direct determination of water in milk.

*Hydrogen Dioxide*.—E. Schoene§ gives an historical sketch of the several methods employed for the quantitative estimation of hydrogen dioxide, and the results of his own experiments to determine their accuracy. He concludes: 1. That for solutions containing only between .00008 and .001 gr. to the liter his own colorimetric method is the best; 2. that for more concentrated solutions the potassium permanganate volumetric method is accurate; 3. that, next to this, the iodo-acidimetric method of Houzeau is to be recommended; 4. that the gasometric method of Thenard and the iodometric of Brodie are inferior to any of the preceding, both in respect to accuracy and convenience; 5. that it is still uncertain whether indigo can be employed for an exact quantitative estimation of hydrogen dioxide.

*Chlorine*.—H. Schiff|| calls attention to and highly commends an old but not widely known method devised by Piria for the analysis of halogen organic compounds. Piria directed that a small platinum crucible containing the substance and filled with black flux be covered by inverting over it another somewhat larger, and the pair then again inverted, the space between them filled with the flux, and heat applied. The method could not be employed for the analysis of compounds containing nitrogen, in consequence of the formation of cyanide of potassium. Schiff, however, fully obviates this difficulty by using a flux consisting of one part of anhydrous sodium carbonate and four or five parts of lime.

To detect or determine chlorine in animal fluids without destruction of the organic matter by combustion, J. Latschenberger and O. Schumann¶ treat a quantity of the fluid with at least an equal volume of a saturated solution of copper sulphate, dilute with water, exactly neutralize with caustic soda, dilute again, filter, and proceed as usual with solutions containing only inorganic matter. This process does not succeed with solutions containing grape-sugar.

*Bromine*.—H. J. H. Fenton\*\* gives further results of his investigation on the actions of sodium hypochlorite and hypobromite on some nitrogen compounds. Both liberate all the nitrogen of ammonium salts, two-thirds that of guanidine, and one-third that of binret, while neither decompose the cyanates. The latter liberates all the nitrogen contained in ammonium carbonate and urea, the former only one-half.

W. Foster,†† on the other hand, finds that a solution of alkaline hypobromite liberates only about 92.5 per cent. of

\* Jour. prak. Chemie, 19, 223.

† Dingler's polytech. Jour. 231, 56.

‡ Liebig's Annal. d. Chemie, 195, 293.

\*\* Jour. Chem. Soc. 1879, 12.

† Jour. prak. Chemie, 19, 401.

§ Zeitsch. anal. Chemie, 18, 183.

¶ Zeitsch. physiolog. Chemie, 3, 161.

†† Jour. Chem. Soc. 1879, 119.

the nitrogen contained in urea: He infers from his experiments that the residual 7.5 per cent. is converted into cyanate.

*Iodine*.—A. E. Menke\* believes that the yellow coloration observed when strong solutions of sulphurous acid and potassium iodide are mixed is due to the formation of iodide of sulphur.

“On the Conduct of concentrated Iodide of Potassium solutions towards Sulphide of Hydrogen,” by E. Schering.† See note on page 71 of this Journal, Vol. I.

To separate chlorine, bromine and iodine quantitatively, A. Guyard‡ acidifies the solution containing them with sulphuric acid; adds bisulphite of sodium and sulphate of copper; treats the filtrate from the enprous iodide, after expulsion of the sulphurous acid, with bichromate of potassium and sulphuric acid; distills the bromine into carbon bisulphide, a solution of sulphurous acid, a sulphite or iodide of potassium, according to the method to be used in its determination; and, finally, precipitates the chlorine as chloride of silver after having reduced the excess of bichromate of potassium by means of a sulphite.

*Fluorine*.—“On a new Volumetric Method of determining Fluorine,” by S. F. Penfield. See this Journal, Vol. 1, p. 27.

“On the Conduct of Silicates containing Fluorine at high Temperatures,” by C. Rammelsberg.§

*Sulphur*.—R. Otto|| recommends that the sulphide of hydrogen employed to detect arsenic in cases of suspected poisoning, be prepared by treating calcium sulphide with pure hydrochloric acid.

Ad. Carnot¶ directs attention to the fact that Ebelmen long ago advocated the use of sulphide of hydrogen in the dry way in analyses involving the separation of metals whenever a part of the sulphides, which would be thus produced, are volatile and a part non-volatile, or a part soluble in weak acids and a part insoluble. In order to render the method useful for quantitative determinations, the author has undertaken to ascertain which metals give sulphides of constant composition when their compounds are heated in a Rose's crucible in a current of dry sulphide of hydrogen; and finds that manganese, zinc, nickel, silver, lead, bismuth, antimony, tungsten and molybdenum, yield sulphides of constant composition, namely,  $\text{MnS}$ ,  $\text{ZnS}$ ,  $\text{NiS}$ ,  $\text{AgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{WS}_2$  and  $\text{MoS}_2$ ; while iron, cobalt, copper and tin do not.

Ph. de Clermont\*\* gives the results of his experiments on the decomposition of metallic sulphides by salts of ammonium. A boiling solution of chloride of ammonium does not attack the sulphides of bismuth, copper, cadmium, platinum and

\* Chem. News, No. 998, 19.

† Bull. de la Soc. Chim. 31, 301.

‡ Ber. d. chem. Gesell. 12, 215.—See note Vol. 1, p. 68 this Journal.

¶ Comptes rendus, 89, 167.

+ Ber. d. chem. Gesell., 12, 156.

§ Pogg. Ann. 8, 146.

|| Ber. d. chem. Gesell. 12, 215.—See note Vol. 1, p. 68 this Journal.

\*\* Bull. d. Soc. Chim. 31, 483.

mercury, but completely decomposes those of antimony and tin, with formation of chloride of antimony, stannic acid, or stannous oxide. It dissolves the sulphides of nickel, cobalt and zinc, somewhat slowly; of iron and manganese, on the other hand, rapidly and completely. Since the hydroxides of aluminum and chromium are insoluble in chloride of ammonium, the author proposes to make use of this reagent to separate them from iron and manganese.

J. Grossmann\* determines the amount of sulphurous and hyposulphurous acids in solutions free from sulphates and sulphides, by ascertaining the amount of iodine required for their conversion into sulphate and tetrathionate, and the wt. of sulphate which they yield on complete oxidation. Having obtained these data, the following equations—supposing the acids to be present as sodium salts—enable one to obtain the quantities sought:

$$x + y = A \text{ and } \frac{2\text{Na}_2\text{SO}_3}{I} x + \frac{\text{Na}_2\text{SO}_4}{2I} y = B,$$

in which  $x = I$  required by  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $y = I$  required by  $\text{Na}_2\text{SO}_3$ ,  $A = I$  required by  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_3$ , and  $B = \text{Na}_2\text{SO}_4$  found. If a sulphide is present, it is removed by means of cadmium carbonate. If the solution contains sulphate, it is placed in a flask, treated with  $\text{HNaCO}_3$ , the air displaced by  $\text{CO}_2$ ,  $\text{HCl}$  added, the  $\text{SO}_2$  expelled by heat, and the  $\text{H}_2\text{SO}_4$  determined as  $\text{BaSO}_4$  in the filtrate.

A. G. Haddock† recommends the use of a small glass mirror instead of the usual black glass plate in the volumetric estimation of sulphuric acid by means of barium chloride.

B. Delachanal and A. Mermet‡ claim that the method of Fahlberg and Iles§ for the determination of sulphur is essentially the same as that formerly described by them.||

*Nitrogen.*—W. Hankó: "A new Modification of Simpson's Method of determining Nitrogen."\*\*¶

J. Ruffle: "On Total Estimation of Nitrogen by Combustion."\*\*\*

H. Schiff: "On the Analysis of Organic Compounds containing Nitrogen."††

E. Pflueger: "A new Method of Analysis of Organic Compounds containing Nitrogen."‡‡

A. R. Leeds§§ confirms the statement of F. H. Storer that solutions of ammonium chloride undergo partial nitrification when kept for some months in a dark place.

S. W. Johnson and E. H. Jenkins|||: "Determination of Nitrogen, &c."

\* Zeitsch. anal. Ch. 18, 79.

† Bull. d. Soc. Chim. 32, 50.

‡ Annales de Phys. et de Chim. 12, 88.

\*\* Chem. News, 40, 17.

†† Zeitsch. anal. Chemie, 18, 296.

† Chem. News, 1011, 156.

§ Ber. d. chem. Gesell. 11, 1187.

¶ Ber. d. chem. Gesell. 12, 451.

‡‡ Liebig's Annal. d. Chem. 195, 293.

§§ Chem. News, 39, 17.

||| This Journal, 1, 72.

To determine the total nitrogen in manures containing nitrates by means of Will-Varrentrap's method, A. Rémont\* mixes with the material to be analyzed a quantity of powdered white sugar equal in weight to about ten times the nitrates supposed to be present.

R. R. Tatlock† calls attention to the fact that when guano is heated with soda-lime for the purpose of estimating the ammoniacal nitrogen, a part of the nitrates are converted into ammonia in consequence of the presence of organic matter; and hence, that too high results are obtained by adding this nitrogen to that found by a separate determination of the nitrates.

Mawson and Swan‡ give a description of Lunge's nitrometer for the determination of nitrous and nitric acids.

R. Warrington§ publishes the results of the experiments undertaken by him to test the accuracy of the Crum-Frankland method of determining nitric acid as nitric oxide by means of mercury. His conclusions are: 1. That, in the absence of organic matter, the method is one of great accuracy; 2. that the natural error is a small one of deficiency; 3. that the presence of chlorides is no hindrance to its success; 4. that small quantities of organic matter have little or no effect on the result, while large quantities, especially of cane sugar, may cause a considerable deficiency. The presence of chlorides tends to diminish, but does not wholly remove, the error caused by the presence of organic matter.

"On the Titration of Sulphuric and Nitric Acids for Hypo-nitric Acid," by A. R. Leeds.||

"On the Detection and Estimation of Nitrous Acid in potable Waters, Acids, &c.," by A. R. Leeds.¶

W. Schroeder\*\* finds that when urine is treated with an acid and quartz or gypsum, and evaporated on the water-bath, the same quantity of nitrogen is obtained from the residue as when the evaporation is conducted under the air-pump, as recommended by C. Voit.†† The author has made some determinations of nitrogen in urine by Seegen's method,‡‡ but his results do not tend towards the establishment of its reliability.

*Phosphorus*.—According to J. Riban§§ a solution of cuprous chloride in hydrochloric acid may be used with advantage for the determination of phosphide of hydrogen in gaseous mixtures. The product first obtained is a colorless crystalline compound having the formula  $\text{Cu}_2\text{Cl}_2\cdot 2\text{PH}_3$ , which, however, dissolves on treatment with an excess of the gas.

Some time ago H. Albert and L. Siegfried||| proposed to

\* Bull. de Soc. Chim. 31, 242.

† Chem. News, 39, 183.

‡ Jour. Americ. Chem. Soc. 1, 18.

\*\* Zeit.-ch. physiolog. Ch. 3, 70.

†† Zeitsch. anal. Ch. 3, 155.

||| Zeitsch. anal. Ch. 16, 182.

† Chem. News, 39, 268.

§ Jour. Chem. Soc. 1879, 375.

¶ Jour. Americ. Chem. Soc. 1, 136.

†† Zeitsch. anal. Ch. 7, 398.

§§ Bull. d. Soc. Chim. 31, 385.

employ the tartrate of ammonium for separating the reverted phosphoric acid in commercial manures from the insoluble phosphates, instead of the citrate as recommended by Fresenius, Neubauer and Luck. They find, however, on further investigation, that the citrate is to be preferred.\* Johnson and Jenkins, on the other hand, state that some experiments of their own, not yet completed, lead them to hope that the tartrate may be successfully substituted for the citrate.† These authors‡ give, also, their mode of procedure to determine phosphoric acid in fertilizers, which consists of separating the phosphoric acid from iron and aluminum by Otto's method, and subsequently determining it by Stolba's.§ The results thus obtained agree very closely with those obtained by the molybdate of ammonium method.

H. Gilbert|| calls attention to the fact that to determine phosphoric acid volumetrically in the so-called ammonia superphosphates, it is necessary to add a corresponding quantity of ammonium sulphate to the solution of phosphate by which the value of the standard solution of uranium salt is determined.

A. Pavce¶ determines the phosphoric acid in a portion of superphosphate gravimetrically, and then employs the superphosphate itself to ascertain the value of his uranium solution.

Other articles relating to the quantitative determination of phosphorus have appeared under the following titles: "On the Determination of Phosphoric Acid in Fish Guano," by B. E. Dietzell and M. G. Kressner.\*\* "Determination of Silicon and Phosphorus in Iron and Steel," by A. A. Blair.††

*Arsenic.*—According to W. Johnstone,‡‡ the discovery of the fact that arsenic and antimony can be separated by the action, in their presence, of potassium hydroxide upon aluminum, did not originate with O. Johnson,§§ but with Prof. Filhol.

Under the title of "Critique of the former Method of Bunsen for the Separation of Arsenic from Antimony," L. F. Nilson|||| gives a resumé of the facts developed by a previous examination of the method, which tended to show its unreliability;¶¶ and then replies to Bunsen's criticism of his work\*\*\* by showing that the separation is imperfect even when the directions of Bunsen are carefully followed.

*Antimony and Bismuth.*—"Certain characteristic Color-Reactions produced by the Action of Aromatic Hydrocarbons and the Vegetable-Alkaloids on fused Antimony and Bismuth Trichlorides," by W. Smith.†††

*Silicon.*—"On the Determination of Silicon in Pig Iron and Steel," by T. M. Drown.‡‡‡

\* Zeitsch. anal. Ch. 18, 230.

† This Journal, 1, 84.

‡ Ber. d. chem. Gesell. 12, 271.

\*\* Zeitsch. anal. Ch. 18, 225.

†† Chem. News, 39, 32.

‡‡ Zeitsch. anal. Ch. 18, 165.

\*\*\* Liebig's Ann. d. Ch. 192, 305.

† This Journal, 1, 86.

§ Zeitsch. anal. Ch. 16, 100.

¶ Zeitsch. anal. Ch. 18, 360.

†† Zeitsch. anal. Ch. 18, 122.

‡‡ Chem. News, 38, 301.

§§ Zeitsch. anal. Ch. 16, 417.

¶¶ Chem. News, 70, 26.

‡‡‡ This Journal, 1, 147.

*Carbon*.—L. Klein\* finds that Classen's modification of the Fresenius-Kolbe apparatus† can be employed with advantage for the purpose of determining carbon in pig iron, in the place of that devised by Ullgren.‡

H. N. MORSE.

[To be continued.]

#### THE SUBSECTION OF CHEMISTRY AT SARATOGA.‡

On the 27th of August, 1879, the American Association for the Advancement of Science met at Saratoga. Over two hundred and fifty members were in attendance, and of these a far larger proportion than usual were chemists. The subsection of chemistry, therefore, hitherto a decidedly minor feature of the Association, sprang into unwonted prominence, and fairly divided interest with the older and stronger sections, A and B.

In the absence of Professor Remsen, the regular chairman for the year, the subsection re-elected Professor F. W. Clarke of Cincinnati to fill the position thus vacant; and Professor W. R. Nichols of the Massachusetts Institute of Technology was appointed secretary. The manuscript of Professor Remsen's address was, however, received, and was read before the whole of section A by Professor Nichols. It was in substance, briefly, a strong plea for the more thorough study in our country of modern organic chemistry; based partly upon practical and partly upon theoretical considerations.

The real work of the subsection began on Thursday, with a series of papers by Professor A. R. Leeds of Hoboken. The following short notes will give an idea of their character.

*"Action of ozone upon the coloring matter of plants."*—In this paper Leeds described the exposure of various leaves and colored flowers to ozone. Bleaching took place, as was to be expected; but a considerable percentage of ozone was required to effect it. When such small amounts were employed as are commonly obtained with the phosphorus ozonator, a large volume of air was necessary and a considerable period of time.

*"Bleaching of sugar syrups by ozone."*—That such bleaching could be effected was not new; but it was shown in this paper that it was readily performed, and that the operation was not attended by any formation of inverted sugar.

*"Reduction of carbonic acid by phosphorus at ordinary temperatures."*—In certain investigations Professor Leeds found it necessary to ascertain whether or no phosphorus could exert any action upon carbonic acid; a negative result being

\* Zeitsch. anal. Ch. 18, 76.

† Zeitsch. anal. Ch. 15, 288.

‡ Liebig's Ann. d. Chemie, 124, 59.

§ Communicated at the request of the Editor.

confidently expected. Accordingly, fresh phosphorus was put under water in three ozonators, and the air was then thoroughly expelled by a stream of carbonic acid. The discs upon which the sticks of phosphorus rested were now raised so as to bring the latter in contact with the stream of gas, and abundant reactions for carbonic oxide were speedily obtained. In a second experiment two flasks were filled with carbonic acid, there being at the bottom sticks of phosphorus partly covered by water. Again carbonic oxide was copiously formed. Incidentally to this reaction, phosphuretted hydrogen was produced. In the absence of carbonic acid, this substance did not appear. When water which had been previously boiled to expel air was digested for forty-eight hours with phosphorus at a temperature of  $92^{\circ}$  to  $96^{\circ}$ , not a trace of phosphuretted hydrogen could be detected. The reaction with the carbonic acid was probably as follows:



In immediate connection with this paper Professor Leeds presented a fourth one, entitled "*Oxidation of carbonic oxide by air over phosphorus at ordinary temperatures.*" In this investigation a mixture of air and carbonic oxide was exposed over moist phosphorus. By the action of the nascent ozone carbonic acid was formed.

A fifth paper by Leeds, "*On the solubility of ozone in water,*" was read before the whole of section A on Friday morning. After a critical historical resumé, the reader described experiments to show whether lead plates immersed in aerated and in ozonized water were oxidized differently; whether lead sulphide would be changed into sulphate; and whether silver under like conditions could be peroxidized. Plates of lead, of lead coated with sulphide, and of silver, were immersed in water one centimeter below the surface; and over the surface a stream of thoroughly washed ozonized air was passed. The experiments were varied considerably, but the final results may be concisely summed up thus: The lead was oxidized upon its surface to hydrated monoxide. The lead sulphide was transformed into lead dioxide and free sulphuric acid. The silver was strongly corroded. Hence the ozone, as such, must have been to a certain extent absorbed by the water, beneath which the foregoing substances were attacked. This fact being established, probably Carius' results as to the quantity of ozone soluble in water may be accepted as correct.

Three other papers came before the chemical subsection on Thursday. First, a paper entitled "*Household Chemistry,*" by Mrs. Ellen H. Richards. This was essentially an earnest argument in favor of the study of chemistry by women, and was warmly endorsed by several members in the brief discussion which followed it.

Prof. W. R. Nichols came next in order with a paper, "*On the deterioration of library bindings.*" In a series of analyses of crumbling and decaying leather bindings the author had found unusually large proportions of sulphuric acid; in one instance over eight per cent. This acid he regards as the cause of decay, and, with other chemists, is inclined to attribute its presence to the sulphur in coal gas. The paper, which is to be regarded as a report of progress in the investigation of a much-discussed and still unsettled question, will probably appear in full in the *Library Journal*.

The closing paper on Thursday was by Prof. H. W. Wiley, of Purdue University, on the "*Percentage of sugar in the sap of the sugar maple, and causes which determine its variation; with note on the pressure of sap.*" At the close of the last sugar-making season, which was a poor one, Prof. Wiley began his analyses, using one of the new polariscopes made by Schmidt and Haensch in Berlin. On March 21st, at the beginning of a thaw after a sharp freeze, specimens of sap were taken from twelve trees representing in general the average of the grove. On March 25th, after two days' continuous run, a second series of specimens was taken. The following numbers represent the percentage of sugar in each sample:

		March 21st.	March 25th.
1.	...	3.95	3.44
2.	...	2.95	2.63
3.	...	3.26	2.80
4.	...	2.70	2.34
5.	...	2.70	2.60
6.	...	3.20	2.42
7.	...	2.51	2.00
8.	...	1.95	1.87
9.	...	3.08	2.00
10.	...	2.67	2.34
11.	...	2.70	2.11
12.	...	3.51	2.74

Hence a long-continued flow of sap diminishes the percentage of sugar. A so-called "sweet tree," famous for the quality of its sap, growing on limestone soil in Southern Indiana, gave a sugar percentage of 4.30 at the end of the season. Such "sweet trees" have in general very dark-colored bark. Trees which have been long in use do not yield a sugar as easily crystallizable as that given by younger trees. The investigation is to be continued next spring.

On Friday but three papers were given before the subsection of chemistry. First, "*Observations on the variations in the temperature and chemical character of the water of Fresh Pond, Mass.,*" by W. R. Nichols. This communication was essen-

tially a report of progress, and was not in any way suited for abstraction. It called out, however, considerable discussion, in which pretty nearly the whole ground of variations in water, and water analysis, was gone over. The discussion was mainly a comparison of views rather than an actual argument, and in it Profs. Silliman, Brewer, Leeds, Peckham, Perkins and others took part. A great deal of interest was manifested in the subject, and the members present seemed unanimously to consider the time devoted to it as unusually well spent.

The two other papers of Friday were by Prof. A. A. Breneman of Cornell University. The first of these — "*On the combustion of graphite in analyses of cast iron*" — described certain improvements which could be rendered intelligible only by a diagram or plate, and which were illustrated to the audience both upon the blackboard and by the exhibition of the apparatus itself. The other was entitled "*On colors for salt-glazed pottery*." In the decoration of such ware the only pigment commonly used is the ordinary cobalt blue. The various tints of brown employed for common stoneware are "slip" colors of fusible clay, and are not salt-glazed, the effect of salt upon them at high temperatures being to cause decoloration by volatilizing the iron as ferric chloride. The tints of pink and green recently shown by Doulton of Lambeth are suited only to the finely decorated pottery known as "Doulton ware." In order to increase the list of colors available for salt-glazed pottery, Prof. Breneman made a series of experiments upon clay tiles in an ordinary stoneware kiln, using all of the common metals capable of coloring fluxes, and also some of the rarer ones like vanadium and molybdenum. Most of his results were simply negative, because of the volatility of the metallic chlorides formed. A few of the results, however, deserve mention. Uranium yellow (sodium uranate), which has long been employed in decorating porcelain, answers admirably for salt-glazed ware if finely powdered before using. It does not fuse, but adheres firmly, takes the glaze, and yields an orange yellow more brilliant than the original color. A mixture of two parts of potassium dichromate, six of borax and one of boric acid, fused and powdered, gives a good brown which takes the glaze perfectly. As borax is apt to "craze" the glazing, the above may be improved by replacing half of that substance by sodium carbonate and omitting the boric acid. Chromic oxide yields better results than the dichromate, and by varying its proportions any shade of brown may be obtained. Solutions of platinic chloride give warm grays, and solutions of gold chloride afford delicate tints of pink. Finely divided gold tends to gather into buttons of metallic appearance. Prof. Breneman exhibited specimen tiles to show the colors produced, and stated his intention of carrying the experiments farther.

Saturday's session of the subsection began with two papers upon gas analysis, entitled as follows: "*A modified method of collecting and measuring gases soluble in water*," by H. W. Wiley; "*Details of the construction of an apparatus for the analysis of gases*," by E. W. Morley. As these papers necessarily dealt with experimental details, neither could be rendered intelligible without drawings. They were followed by Mrs. E. A. Smith of Jersey City, who gave an interesting popular account of the great Oberstein industry of cutting, polishing, and artificially coloring agates, and other similar stones. A very beautiful collection of specimens was used to illustrate the paper. After this, a joint communication was presented by W. L. Dudley and F. W. Clarke, describing graphite from the Ducktown copper mine in Tennessee. The mineral mass under discussion was a complex mixture of graphite, copper pyrites, and various silicates. The purest graphite which could be selected from the specimen gave nearly 68 per cent. of carbon, and the ash had approximately the composition of an iron epidote, with the oxygen ratios  $RO : 2R_2O_3 : 3SiO_2$ . Graphite has never before been reported from this locality. A short note by J. W. Osborne "*On a peculiar case of corrosion of the metal tin*," came next, followed by the closing paper of the day's session, "*A preliminary notice of a revision of the atomic weights*," by F. W. Clarke.

The writer, having collected all the published weighings relative to atomic weight determinations, has undertaken their complete recalculation and recombination from the bottom up. He begins with oxygen, for which the atomic weight has been ascertained by the synthesis of water over copper oxide, and by the relative densities of hydrogen and oxygen gases. In the copper oxide method we have nineteen experiments by Dumas, and eight by Erdmann and Marchand. Dumas' results give a mean of 15.9607, with a probable error of  $\pm .0071$ . Erdmann and Marchand's mean is 15.9733;  $\pm .0113$ . These two means, combined by the usual formula, give a general mean of 15.9642;  $\pm .006$ , as the most probable value for the atomic weight of oxygen as ascertained by this method. From the relative densities of oxygen and hydrogen, Regnault's figures, the only series worth considering, give us  $O = 15.9628$ ;  $\pm .0043$ . By combining this value with the other, we get a final general mean of  $O = 15.9633$ ;  $\pm .0035$ . This value is of course involved in all the subsequent atomic weight calculations, and its probable error affects necessarily all the other probable errors. After oxygen, the elements silver, potassium, sodium, chlorine, bromine, iodine, and sulphur, are discussed in a group. To begin with, all similar data are reduced as far as possible to common standards. For example, there are nine series of determinations of the percentage of oxygen in potassium chlorate. For each series

the mean was calculated, and its probable error; and the nine means were then combined by the ordinary method into one general mean. Thus all the data relative to the seven elements in question were condensed into twenty ratios; and from these, eight independent values for the atomic weight of silver could be deduced. The general mean of these eight values is  $\text{Ag} = 107.675; \pm .0096$ . In this group of elements data were considered from Berzelius, Penny, Pelouze, Marignac, Mauméné, Gerhardt, Millon, Struve, Svanberg and Struve, Turner, Dumas, Cooke, and Stas; each series of experiments receiving exactly the weight indicated by the probable error of its mean. The final results were as follows, if  $\text{O} = 15.9633; \pm .0035$ .

Ag	=	107.675; $\pm .0096$
Cl	=	35.370; $\pm .0145$
Br	=	79.768; $\pm .019$
I	=	126.557; $\pm .022$
Na	=	22.998; $\pm .011$
K	=	39.019; $\pm .012$
S	=	31.984; $\pm .012$

It is interesting to compare these results with those obtained by Stas alone. Since the latter took for oxygen the atomic weight of sixteen, the figures are comparable only when the new numbers are recalculated by the same standard. We then get the following table:

		New Values.	Stas.	Difference.
Ag	...	107.923	107.930	.007
Cl	...	35.451	35.457	.006
Br	...	79.951	79.952	.001
I	...	126.848	126.850	.002
Na	...	23.051	23.043	.008
K	...	39.109	39.137	.028
S	...	32.058	32.074	.016

These differences, it will be seen, are far within the limits of experimental errors; and the table emphasizes in the most forcible way the magnificent accuracy of Stas' work. No other researches than his could stand so severe a test. At the present date the writer has finished his calculations for forty-three of the elements; and he hopes before long to complete and publish the entire investigation.

On Monday, September 1st, the subsection of chemistry completed its season's work. The session was opened by Professor E. W. Morley, with a striking paper upon "*Results of systematic analyses of air, designed to discover the cause of variations in the quantity of oxygen therein contained.*" This com-

munication, which has appeared in full in the "American Journal of Science and Arts" for September, may be summed up for present purposes very briefly. Professor Loomis has suggested that the so-called "polar waves" may be really sudden vertical descents of cold air from very great elevations. Since oxygen is heavier than nitrogen, it is mathematically probable that air at a great height would be poorer in the former gas than that at ordinary levels. If this be true, and Loomis' theory is correct, then the air which has suddenly fallen upon us during a severe cold snap should contain less oxygen than the average. That this is actually so, and that the variation is far within the limits of experimental error, Prof. Morley has shown; thus confirming in a most curious way the views of Professor Loomis. The investigation is to be carried yet farther, and with additional refinements in the methods of analysis.

Professor W. R. Nichols next gave a brief statement of "*An accidental contamination of a source of water supply.*" This related to a fire near Boston, in which large quantities of sulphuric acid from a burning building flowed into certain bodies of water used to supply parts of the city. The results showed the insignificant effect produced by the contamination.

The next paper, by William McMurtrie of the Agricultural Department at Washington, was only partially chemical, and unfortunately not suited for abstraction. It was entitled "*The limits of meteorological conditions governing the extension of beet root culture*"; and it will appear in full as part of a government report. It was followed by A. A. Breneman, "*On the action of caustic alkaline solutions upon glass.*" In the author's absence, this paper was read only by title. In substance, the communication is as follows: A number of large, green glass bottles were used in the laboratory of Cornell University for holding weak solutions of caustic soda. These bottles were frequently found to be cracked and leaking. Examination showed that minute cracks started from the inner surface of the glass, and slowly developed outward. The explanation suggested is that the thicker portions of the glass were left by imperfect annealing in a state of strain or tension; and that the removal by the caustic soda of small portions of the inner surface disturbed the equilibrium of molecular forces, and led to local rupture.

The closing paper of all was by Professor C. Gilbert Wheeler of Chicago—"A chemical examination of black ozokerite."

The subsection elected as its officers for next year, Prof. J. M. Ordway of Boston, chairman; and Professor C. E. Munroe of the U. S. Naval Academy, secretary. The meeting of the Association will begin in Boston on the last Wednesday of August, 1880; and it is to be hoped that a large number of working chemists may attend, and present for discussion their best material.

PAPERS READ BEFORE SECTION B (CHEMICAL SCIENCE SECTION) OF THE  
SHEFFIELD MEETING OF THE BRITISH ASSOCIATION.

*W. Chandler Roberts.*—Report of Committee on the Chemistry of some of the lesser-known Alkaloids.

*Walter Weldon.*—On some relations between the numbers expressing the Atomic Weights of the Elements.

*M. R. D. Silva.*—On the Synthesis of Diphenyl-propyl.

*F. A. Abel.*—Recent Researches in explosive Agents.

*Prof. Dewar.*—On Vapor Densities.

*P. Braham.*—To describe a large Crystal of Mercury Sulphate.

*Henry S. Bell.*—On the Manufacture of Crucible Steel.

*Thomas Blair.*—On the separation of Iron and Phosphorus, especially with reference to the Manufacture of Steel.

*John Hollway.*—A New Process in Metallurgy.

*A. H. Allen.*—A Lecture Experiment in Illustration of the Hollway Process of Smelting Sulphide Ores.

*Andrew French.*—On Lead Fume, with a description of a New Process of Fume condensing.

*Prof. Odling.*—On the Constitution of Aluminic Compounds.

*A. H. Allen.*—On the Presence of Nitrogen in Steel.

*A. Vernon Harcourt.*—Color tests for Phosphorus and Sulphur in Iron and Steel.

*W. Chandler Roberts.*—To exhibit some Experiments with Hughes's Voltaic Induction Balance.

*J. T. Brown.*—Historical sketch of the various Vapor-Density methods.

*Prof. Wanklyn.*—Note on certain Vapor Densities.

*Prof. Wanklyn.*—Note on Isoeyan-propionic Acid.

*G. Ansdell.*—Physical constants of Liquid Acetylene and Hydrochloric Acid.

*M. de Clermont.*—The Action of Ammoniacal Salts of Metallic Sulphides.

*W. Ivison Macadam.*—On the chemical composition of a Nodule of Ozokerite found at Kinghorn-ness.

*Thos. Andrews.*—On some curious concretion Balls derived from a Colliery Mineral Water.

*Dr. Gilbert.*—On some points in connection with Agricultural Chemistry.

*T. S. Humpidge.*—On the rare Metals of the Yttrium group.

*Prof. Dewar.*—On the Synthesis of Hydrocyanic Acid.

*Prof. Dewar.*—On the amount of Nitrous Acid produced in Electric Illumination.

*Prof. Dewar.*—On the Kinoline Bases.

*John M. Thompson.*—An account of some recent Experiments on supersaturated Solutions.

*J. Norman Lockyer.*—Notes of some recent Spectral Observations.

*A. H. Allen.*—Notes on Petroleum Spirit or Benzoline.

*A. Vernon Harcourt.*—On the Illuminative Value of a Mixture of Hydrogen.

*G. T. Hazelhurst.*—On a new Form of Condenser.

*W. Thompson.*—Notes on a sample of Fuller's Earth found in an old Fullonica recently excavated at Pompeii.

*W. H. Watson.*—On the Detection of Milk Adulteration.

*Dr. Phipson.*—Chemical Researches on the *Palmella cruenta*.

*Philip Braham.*—Description of a glass Burette for collecting, measuring and discharging Gas over Mercury.

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CHEMISTRY: GENERAL, MEDICAL, AND PHARMACEUTICAL, INCLUDING THE CHEMISTRY OF THE U. S. PHARMACOPOEIA. A MANUAL OF THE GENERAL PRINCIPLES OF THE SCIENCE, AND THEIR APPLICATIONS IN MEDICINE AND PHARMACY. By John Attfield, M. A. and Ph. D. Eighth edition, revised by the Author. 697 pp. Philadelphia: H. C. Lea.

This work has passed through seven large editions, and appears now for the eighth time within a period of twelve years. In looking for the cause of its popularity, we think it can be found in the fact that, in connection with all the principal chemical substances described, simple, easily followed directions are given, which enable the student to verify every statement by actual experiment. The fundamental idea of the author, and one which he has successfully followed, is expressed in his own words thus: "A good knowledge of chemistry may be acquired synthetically, by preparing considerable quantities of the salts of the different metals, or analytically, by going through a course of pure qualitative analysis. But the former plan demands a larger expenditure of time than most students have to spare, while under the latter system they generally lose sight of the synthetical interest which attaches to analytical reactions. Hence the more useful system, now offered, of studying each metal, etc., from both points of view, time being economized by the operator preparing only small specimens of compounds."

"Chemical synthesis and analysis, thoughtfully and conscientiously followed, will insensibly carry the principles of chemistry into the mind, and fix them there indelibly."

The practice of making small quantities of a large number of representative chemical substances is an excellent one, and should be more general in all laboratories in which chemistry is taught. The tendency to limit instruction to analysis is very extended. When the relations of the six groups into which the elements are usually divided for analytical purposes are mastered, the end is regarded as reached. We cannot but believe that it would be a great gain if much more attention were given to the synthetical side of the subject; and Dr.

Attfield does instructors in chemistry a real service in showing how this result can easily be reached.

While expressing entire approbation of the general principle adopted in the book, we must beg leave to differ from the author when he believes it advisable to select for study, even for medical and pharmaceutical students for whom the book is written, such substances as are of especial importance in medicine and pharmacy. He is right when he says: "The truths of chemistry are the same for all students—crystalline verities which cannot be expanded or compressed to suit any class of workers." These truths are first to be taught, and should be taught by the readiest methods. If, to illustrate a chemical truth, substances which are of especial importance in medicine can just as well be selected, there can be no objection to selecting them. But when substances are selected simply because they are of importance in medicine, and they do not serve the purpose for which they are selected as well as simpler ones which are neglected, then we believe a serious mistake is made. It so happens that a large proportion of pharmaceutical preparations are comparatively complicated chemical substances, the chemistry of which cannot well be understood by the beginner; hence it would be much better to attempt first to teach the general principles of chemistry through substances best adapted to this purpose without any reference to their applications, and then give a subsequent treatise on pharmaceutical substances. Not to go too much into detail, we call attention to the case of lead, pp. 209–215, as illustrating the objectionable method of the author. The salts of this metal described are the acetate, oxyacetate, nitrate, iodide and oleate! It would be difficult to select more awkward examples for a beginner than the oxyacetate and the oleate. In connection with the latter, too, we find a brief description of the action of lead oxide on olive oil.

Another serious objection which may justly be made to the book is, that the subdivision under the heading "Chemistry of Organic Substances" is written without reference to the simplest recognized principles of organic chemistry. The subject is introduced by a description of the alkaloids, a large amount of space being given to the consideration of morphine, quinine, strychnine, &c. The next group of bodies taken up is that containing starch, and the different kinds of sugar. This part of the book could never have been written by one who has a comprehension of the principles of modern organic chemistry, and ought certainly to be entirely rewritten if the book reaches a ninth edition.

While, from what has been said, it is plain that we cannot conscientiously recommend Dr. Attfield's book to the beginner, it is certain that he has brought together a great deal of useful material, and has succeeded in making a very good book of reference for the medical practitioner and the druggist.

*BOOKS RECEIVED.*

Elements of Modern Chemistry. By Adolph Wurtz. Translated by Wm H. Greene, M. D. Philadelphia: J. B. Lippincott & Co.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the collateral branches. By George Lunge, Ph. D., F. C. S., Professor, &c. London: John Van Voorst.

Supplement to a Handbook of Chemical Manipulation. By C. Greville Williams, F. R. S. London: John Van Voorst.

Experimental Researches in Pure, Applied and Physical Chemistry. By E. Frankland, Ph. D., D. C. L., F. R. S. London: John Van Voorst.

Twenty Lessons in Inorganic Chemistry. By W. G. Valentin, F. C. S. New York: G. P. Putnam's Sons.

Jahresbericht ueber die Fortschritte auf dem Gebiete der reinen Chemie. Ludwig Medicus und W. Staedel. Tuebingen: Laupp.

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*NOTES.*

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*Spectroscopic Investigations.*

As previous researches of G. L. CIAMICIAN have shown, chemically related elements have homologous spectra; that is, the individual spectra of the elements of any given group differ from one another only in having their lines displaced towards one end or the other of the spectrum. In the course of a comparative investigation of the spectra of the metals of the alkaline earths, Ciamician has observed phenomena which are adapted to furnishing an explanation of these remarkable relations between the spectra of related elements. When the spectra of the metals of the alkaline earths are produced by allowing the induction spark to pass between the metals (as electrodes) with inserted Leyden jar in an atmosphere of hydrogen, spectra are obtained which show the homology of the lines very beautifully. The spectrum of magnesium, however, can not be compared with the spectra thus obtained, because it does not contain the less refrangible lines. If the jar is removed, or if a weaker battery and a smaller induction

coil is used, all the lines in the red and yellow field in the spectra of calcium and strontium become less intense, and spectra are obtained which are very similar to that of magnesium. If the less refrangible part of the spectrum of the group of the metals of the alkaline earths—that part which is visible only at a high temperature, corresponding to a high electric tension—is compared with the less refrangible half of the complete oxygen spectrum, it is noticed that these two half-spectra exhibit a remarkable similarity (homology). From this it would follow that the spectrum of the group of the metals of the alkaline earths appears to be made up of that of magnesium, and of the less refrangible half of the oxygen spectrum. As it is known that the atomic weights of barium, strontium and calcium can be made up of the atomic weight of magnesium and of oxygen ( $24 + 16 = 40$  [calcium],  $24 + 4 \times 16 = 88$  [strontium] and  $24 + 7 \times 16 = 136$  [barium]), experiments were undertaken to discover whether these remarkable relations in the spectra have any real significance. The author has shown that there exists the same kind of relation between the spectra of carbon and of nitrogen and that of cyanogen, and between the spectra of carbon and of oxygen and the spectrum of carbon monoxide, as that observed between the spectra of magnesium and of oxygen and that of the group of the metals of the alkaline earths. It can hence be said that in all probability the homology of the spectrum lines of chemically related elements depends upon the fact that, in accordance with the regularities in the atomic weights noticed by Mendelejeff, the elements of such natural groups consist of the same components.—(*Wiener Sitzungsberichte*, 79, II. Abth.)

#### *Nitrous Oxide as an Anaesthetic.*

PAUL BERT reports the complete success attending the application of nitrous oxide as an anaesthetic in lengthy surgical operations. A mixture of 85 per cent. of nitrous oxide and 15 per cent. oxygen is administered in the same manner as when used by dentists except that the whole operation takes place in a specially constructed chamber where the pressure of the atmosphere can be varied at the will of the operator. Experience shows the agent to be entirely harmless and to possess many advantages over other anaesthetics in practical use.—(*Comptes rendus*, 89, p. 132.)

#### *On the Conduct of Chlorine at high Temperatures.*

In continuing the application of their admirable method for the determination of specific gravities of vapors, VICTOR and

CARL MEYER have discovered some extremely interesting facts regarding chlorine. They have shown that, while, as is well known, the spec. gr. of chlorine at ordinary temperatures conforms to the law of Avogadro, at a temperature a little above  $620^{\circ}$  the spec. gr. becomes somewhat less, and then, as the temperature is raised, there is a gradual decrease in the spec. gr. until at about  $1200^{\circ}$  a minimum is reached. From this point up to  $1567^{\circ}$  the spec. gr. remains constant and corresponds to the formula  $\frac{2}{3}\text{Cl}_2$ . Hence, according to the authors, *the molecular weight of chlorine, which at low temperatures (below  $600^{\circ}$ ) is 71, is 47.3 ( $\frac{2}{3} \cdot 71$ ) above  $1200^{\circ}$ .* In the course of their remarkable paper the authors use these words: "We postpone for the present any discussion of the theoretical conclusions which are suggested by these experiments and which must lead to a new theory of the halogens." They promise, however, to give special attention to two possible explanations which suggest themselves at once. One of these is founded upon the idea that the quantity of chlorine which has hitherto been considered as the atom is a compound of three atoms of a trivalent element of the atomic weight  $\frac{35.5}{3}$ . The other is the old murium theory so often suggested and as often discarded. In testing this latter theory, it is proposed to allow chlorine heated to  $1567^{\circ}$  to diffuse through a diaphragm with the object of separating the possibly compound gas into its constituents.—(*Ber. d. chem. Gesell.* 12, 1426.)

#### *Vapor Density of Chlorine.*

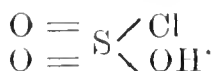
LIEBEN offers the following suggestions as possible explanations of the change at high temperatures of the vapor density of chlorine:

1. It may be that the coefficient of expansion of chlorine above  $700^{\circ}$  is somewhat greater than that of oxygen, nitrogen, sulphur and mercury, the other vapors examined by Meyer. It is known that gases at high pressure vary from the law of Mariotte, and vary unequally. The coefficients of expansion of different gases between  $1200^{\circ}$  and  $1600^{\circ}$  are unknown, and it is not inconsistent to suppose that the coefficient of chlorine may be greater than that of oxygen, nitrogen, &c., above  $700^{\circ}$ , while below  $700^{\circ}$  sensibly equal. If this were the fact, then the vapor density of chlorine referred to air or nitrogen would be less from  $1200^{\circ}$  to  $1600^{\circ}$  than from  $0^{\circ}$  to  $600^{\circ}$ .

2. It may be that the molecule of chlorine ( $\text{Cl}_2$ ) is dissociated at high temperature, and in a certain interval of temperature there may be an equilibrium such that one-half of the molecules of chlorine are dissociated and the density reduced one-third.—(*Comptes rendus*, 89, 353.)

*On Chlor-stannic Acid.*

In a bottle containing a pretty strong aqueous solution of stannous chloride which had stood for a year or two, never very tightly closed, J. W. MALLETT noticed the formation of a soft solid layer of nearly transparent jellylike material. This was washed and allowed to dry at atmospheric temperature. An analysis showed that the substance contained HCl and  $\text{SnO}_2$  in the proportions required by the formula  $\text{O} = \text{Sn} \begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{OH} \end{smallmatrix}$ , or that of normal stannic acid with one hydroxyl replaced by chlorine, analogous in structure to the chloro-hydrated sulphuric acid of Williamson



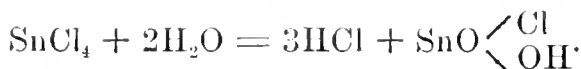
The change experienced by the original stannous chloride may be supposed to have been



or else the usual formation of stannous oxychloride and stannic chloride from absorption of oxygen,



may have first occurred, followed by the reaction



The author calls the new substance chlor-stannic acid.—(*Jour. Chem. Soc.* Aug. 1879, 524.)

# AMERICAN CHEMICAL JOURNAL.

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## ON THE SYNTHESIS OF HELICIN AND PHENOL-GLUCOSIDE.

BY ARTHUR MICHAEL.

In 1837, while examining amygdalin, Woehler and Liebig\* investigated its behavior towards an aqueous solution of emulsin, and found that it decomposed under the formation of grape sugar, benzoic aldehyde and hydrocyanic acid. This is the first instance in which a carbohydrate was known to enter into the composition of an organic body. A short time later, Piria† with salicin, and Stas‡ with phloridzin, demonstrated that these compounds are decomposed by dilute acids, under the formation of grape sugar among other products. Since that time, hardly any class of compounds has been found more numerous, and more widely spread, in organic nature than similar bodies, which are now classed under the generic name of the glucosides.

The glucosides are usually considered as mixed ethers of glucose and their other respective constituents; an hypothesis which explains, in some measure, the simplicity of their products of decomposition. It will be found, however, that many of them present properties which are not strictly in accordance with this hypothesis. I may mention the great

\*Ann. Chem. Pharm. 22, 1. †Ibid. 30, 151. ‡Ann. de Chemie et Phys. 69, 367.

stability of most of the glucosides towards easily reducible metallic salts; a property which certainly would not lead us to presuppose the presence of the aldehyde group of glucose, and which, according to the above mentioned hypothesis, exists in the glucosides unchanged. Again, their remarkable behavior towards dilute acids, and certain ferments, is not in accordance with the properties of any compound known to belong to the ether group.

P. Schnetzenberger\* was the first to publish experiments on the synthesis of the glucosides. He allowed di- and triaceto-glucose to act on the sodium† and lead salts of saligenin and rhamnetin, but he only obtained badly-defined compounds, which appear to have contained glucose as one of their constituents; however, neither the analyses nor the properties of these compounds corresponded with those of the natural glucosides. I have undertaken the synthesis of the glucosides in a different manner; starting from the interesting compound discovered by A. Colley‡ while examining the action of acetylchloride on glucose, and known under the name of acetochlorhydrose. This compound, which presents the rational formula  $C_5H_6Cl(OC_2H_3O)_4CHO$ , I have allowed to act on potassium phenate and potassium salicylite, and have obtained compounds which possess all the characteristic properties of the glucosides.

In the preparation of acetochlorhydrose, I have little to add to the excellent directions given by Colley in his memoir; but will call attention to the fact that a finely powdered glucose is absolutely necessary, and that when 10 gr. of glucose are employed the reaction is not finished in less than 48 hours.

*Action of Acetochlorhydrose on an Alcoholic Solution of Potassium Phenate.*

After numerous experiments, I found the following conditions to yield the most satisfactory results: 27.5 gr. of acetochlorhydrose were mixed with about twice its volume of absolute alcohol, and the solution added to a cold alcoholic solution of 10 gr. of potassium phenate. After a few minutes, a

\*Compt. rend. 69, 350.

†This salt was not analyzed, and after the experiments of Beilstein and Seelheim (Ann. Chem. Pharm. 117, 89), it is doubtful whether it is a derivative of saligenin.

‡Compt. rend. 70, 401.

crystalline precipitate began to separate from the solution, and at the same time a strong odor of acetic ether was noticed. The reaction proceeded very rapidly, and after four or five hours no further separation of the crystalline substance was observed. The solution was then filtered, and the precipitate examined, which proved to consist of potassium chloride, mixed with a small quantity of amorphous organic matter. The filtrate from the potassium chloride was allowed to evaporate in a flat basin by exposure to the air, and left an oily substance, which, after standing several hours, solidified to clusters of concentrically grouped needles. These crystals were then well pressed between bibulous paper, to free them from an oily substance which would, if left, render their purification very difficult, and they were then easily obtained in a pure state by treating with animal charcoal and crystallizing twice from water.

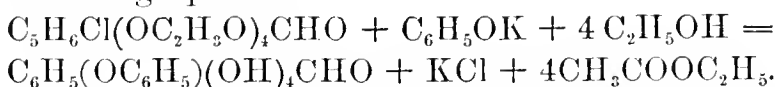
The substance crystallizes from a hot aqueous solution in long, concentrically grouped, odorless, white needles, which melt at 171-172°, and solidify on cooling. It is moderately soluble in cold, and very soluble in warm water. Alcohol and acetic acid dissolve it quite readily in the cold. The aqueous solution has a very bitter taste, and turns the plane of a polarized ray of light to the right.

The most interesting property of this substance is its behavior towards dilute acids and emulsin. A dilute solution of sulphuric or chlorhydric acid decomposes it on gently warming very readily in glucose and phenol: warmed for a short time with an aqueous solution of emulsin the same decomposition is effected. The formation of phenol and glucose was proven by their isolation, and by all their characteristic reactions, and they are the only products of the decomposition; especially, the presence of acetic acid could not be detected. A warm, dilute solution of potassium hydrate decomposes it in a like manner. Concentrated sulphuric acid dissolves it in the cold without decomposition with a yellow color; on the addition of water to this solution, the above mentioned decomposition was observed. An analysis of the compound, dried at 100°, gave: .2112 gr. of substance gave .4385 gr. of CO<sub>2</sub> and .1207 grms. of H<sub>2</sub>O.

		Calculated for $C_{12}H_{16}O_6$ .	Found.
C	...	56.25	56.62
H	...	6.25	6.35
O	...	37.50	37.03

The results of the proximate analysis, and the products of its decomposition, leave no doubt as to the nature of this compound. It is a mixed ether of phenol and glucose, and as its properties correspond entirely with those of the glucosides, although it has never been observed in organic nature, it may be called phenolglucoside.

The constitution of phenolglucoside is expressed by the formula  $C_5H_6(OC_6H_5)(OH)_4CHO$ , and its formation is according to the following equation :



This reaction consists of two parts; one of which, the substitution of the acetyl groups by the hydrogen of the alcohol,\* was not foreseen, although the formation of acetic ether by heating alcohol with tetra-acetohelicin, a fact which was observed by H. Schiff,† several years ago, indicates a similar decomposition of that compound. The facility with which the alcohol acts in this reaction is owing to the fact that the sum of the negative forces acting on each of the oxygen atoms which connect the acetyl groups with the glucose rest, exceeds the negative power of the radical  $C_2H_5O^I$ , and the positive hydrogen atoms of the alcohol, therefore substitutes the negative acetyl groups.

#### *Action of Acetochlorhydrose on an Alcoholic Solution of Potassium Salicylite.*

The properties of phenolglucoside indicate that this compound belongs to the group of natural glucosides, and made it probable that the glucosides obtained by synthesis would not prove isomeric, but identical with those occurring in nature. I have first undertaken the synthesis of helicin, by allowing acetochlorhydrose to act on potassium salicylite.

\*The action of absolute alcohol on the compounds obtained by dehydrating with acetic anhydride, as hexacetatdiglucose, presents considerable interest. I shall also return, in a future paper, to the action of acetylchloride on levulose, and other carbohydrates.

†Ann. Chem. Pharm. 154, 23.

The latter compound was made by adding 1 mol. of salicylic aldehyde to 1 mol. of potassium hydrate dissolved in absolute alcohol, and afterwards adding an equal volume of ether, which caused a further precipitation of the potassium salt. This salt is but moderately soluble in absolute alcohol, 1 part requiring about 20 parts of it.

The action of acetochlorhydroses on this salt was studied under conditions similar to those employed in the synthesis of phenolglucoside. Equivalent quantities of the two substances both dissolved in absolute alcohol, were allowed to react in the cold, and the action was accompanied by the separation of potassium chloride and formation of acetic ether; it proceeded, however, very slowly, and I found it advisable to allow the solution to stand three days before filtering from the potassium chloride. The filtrate was then evaporated by exposure to the air in an open vessel, and left a dark, oily residue, which, after standing ten days, partially solidified. It was well pressed between bibulous paper, and, after repeated treatment with animal charcoal, crystallized three times from warm water.

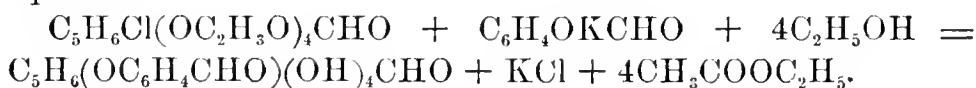
An analysis of the substance, dried at  $100^{\circ}$ , gave results which correspond well with the formula  $C_{13}H_{16}O_7$ . .2100 gr. of substance gave .4206 gr. of  $CO_2$  and .1124 gr. of  $H_2O$ .

		Calculated.	Found.
C	...	54.93	55.09
H	...	5.63	5.90
O	...	39.44	39.11

The compound, therefore, has the empirical formula of helicin, and a comparison of the following properties with those of that glucoside, will show that the two bodies are identical.

When deposited from hot water, it crystallizes in small, white, odorless needles, which contain water of crystallization, and have a bitter taste. It is but sparingly soluble in cold and very readily in warm water; in warm alcohol it is also very soluble, but is insoluble in ether. The crystals melt at  $175$ - $176^{\circ}$  to an olive-colored liquid, which solidifies on cooling: when heated for some time above its melting point, it decomposes with the evolution of salicylic aldehyde, and forms a liquid which solidifies finally to a yellow

resinous mass. The aqueous solution does not reduce silver nitrate or ferric chloride, even on boiling, and is not precipitated by a solution of mercuric chloride or lead acetate. It is easily decomposed by boiling with very dilute sulphuric or chlorhydric acid into glucose and salicylic aldehyde (the presence of acetic acid could not be detected); and under the influence of an aqueous solution of emulsin, when heated at 30°, it undergoes a like decomposition. Dilute alkaline solutions dissolve it in the cold more easily than water, but without change; on boiling this solution it is decomposed as above. A solution of potassio-tartrate of copper does not decompose it in the cold, or even when heated at 50°, but after boiling this solution for several minutes a gradual reduction takes place, doubtlessly owing to the previous formation of glucose. Concentrated sulphuric acid dissolves it in the cold, the solution taking a chrome-yellow color. A drop of this solution placed on a strip of zinc foil, and approached by a drop of distilled water takes a red coloration at the point of contact, owing to the formation of salicin\*. Since helicin has been reduced to salicin†, its synthesis is therefore identical with that of the latter compound. The constitution of helicin or ortho-formylphenol-glucoside, is, therefore,  $C_5H_6(OC_6H_4CHO)(OH)_4CHO$ , and its formation by synthesis is expressed by the following equation:



The synthesis of helicin according to the above described reaction, does not show which of the hydroxyl groups of glucose is the means of connecting the glucose- and salicylic aldehyde-rests; but I may mention here that an investigation of the products which may be obtained by the double decomposition of acetochlorhydrose with numerous reagents, will undoubtedly give a clue to the solution of this problem. Acetochlorhydrose possesses a power of reaction which is only surpassed by that of the acid chlorides; a property which is doubtlessly due to the strong negative character of the body. A better example of its substituting power could hardly be given than the described reactions, which are the first in-

\*H. Schiff, Ann. Chem. Pharm. 154, 26. The action of nascent hydrogen on synthe-  
tical helicin will be studied later more fully, also its and natural helicin's be-  
havior towards a ray of polarized light.

†Lisenko, Zeitschr. Chem. 1864, 577.

stances of a paraffin chloride substituting directly the base of an aromatic phenate in the cold.

I have made several preliminary experiments on the substitution of the chlorine atom of acetochlorhydrose, and which indicate that this compound will permit similar substitution of the glucose radical— $C_6H_6O(OH)_4$ —as the monohaloid derivatives of the paraffins permit with the paraffin radicals. It yields with ammonia, sodium ethylate and sodium aceto-acetic ether defined compounds, and acts on an alcoholic solution of potassium lævulosate with the formation of acetic ether and the separation of potassium chloride; on lævulose itself at  $100^\circ$  with evolution of chlorhydric and acetic acids, forming a small quantity of a new crystalline compound, possibly dextro-lævulose\* or cane sugar.

I called attention in the beginning of this paper to the stability of many of the glucosides towards easily reducible metallic salts; this is the case with helicin, which has just been shown to contain the aldehyde group of glucose unchanged. I do not think that at present any satisfactory explanation can be given for this anomaly, and it therefore remains a fact which is not in accordance with the rational formula of the compound. On the other hand, the ease with which helicin is decomposed by acids will be understood when we consider the facility with which acetochlorhydrose substitutes its chlorine atom; it is owing to the same reason, the negative character of the glucose radical which enters into the composition of the glucoside.

*Action of Acetochlorhydrose on an Alcoholic Solution of Sodium Saligenin.*

The action of metallic sodium on a solution of saligenin in ether yields, according to the experiments of Beilstein and Seelheim,† a sodium derivative of saliretin, and the results I have obtained by the action of acetochlorhydrose on the compound tend to confirm their view.

\* The proof that helicin is an ether of glucose and salicylic aldehyde, notwithstanding its stability towards metallic salts, strengthens the hypothesis of cane-sugar being a mixed ether of glucose and lævulose; since the principal objection against this view is in the much greater stability of cane sugar than glucose towards easily reducible salts, whereas a natural supposition would have given it a greater reducing power, since it contains two aldehyde groups.

† Ann. Chem. Pharm. 117, 89.

Acetochlorhydrose acts on an alcoholic solution of sodium saliretin very readily, forming acetic ether and potassium chloride. The filtrate left on evaporation an oily substance, which solidified to a yellow, gelatinous, bitter mass, soluble in cold water, and which is very probably the glucoside of saliretin, since it is decomposed by dilute sulphuric acid or emulsin in glucose and saliretin.

The above described reaction will probably permit the synthesis of many of the glucosides, and promises to be of considerable interest in those cases in which doubt exists as to the constitution of these compounds, as, for instance, is the case with arbutin. I shall return to this subject in some future paper.

BUFFALO, N. Y., Oct. 11, 1879.

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## ON A NEW FORMATION OF STILBENE AND SOME OF ITS DERIVATIVES.

BY ARTHUR MICHAEL.

The following investigation was made above a year ago, and I had hoped to be able to complete it in a more satisfactory manner, but as there is little probability that I shall in some time be able to return to this subject, I intend to give a short description of the results I obtained, notwithstanding their incompleteness.

W. H. Perkin found, several years since, that by the action of anhydrous sodium acetate on a mixture of benzoic aldehyde and acetic anhydride, the synthesis of cinnamic acid could easily be effected, and generalized this reaction by taking not only different aromatic aldehydes, but also various fatty acid anhydrides. The action of sodium acetate on a mixture of phthalic and acetic anhydrides gives, as Gabriel and myself have shown, a remarkable acid, which we have

called phthalylacetic acid;\* subsequently, we found that the same reagent when used to dehydrate mixtures of phthalic anhydride and organic acids, instead of their anhydrides, always gave ketones;† this was shown to be the case with phenylacetic, succinic and isobutyric acids, and the reaction is doubtlessly much more general. It seemed to me to be of considerable interest to examine the action of dehydrating agents on mixtures of aromatic aldehydes and organic acids, which should give, were the reaction similar to that of phthalic anhydride and acids, unsaturated hydrocarbons, instead of unsaturated acids obtained by the reaction of Perkin.

I first examined the action of sodium acetate on a mixture of benzoic aldehyde and phenylacetic acid, and have obtained stilbene, in this manner, in large quantities. For this purpose, equivalent quantities of benzoic aldehyde, phenylacetic acid and anhydrous sodium acetate, were heated to boiling in an open flask, connected with a condenser, but I found that under these conditions no action ensued. The same mixture was next heated in a closed tube for about 12 hours at 250°, and upon opening the tube it was found to contain a considerable quantity of carbonic acid. The contents of the tube were extracted with boiling water, subsequently with warm dilute ammonia, to remove traces of unchanged phenylacetic acid, and the insoluble residue, which melted under warm water, was treated with animal charcoal, and finally crystallized several times from warm alcohol. The substance,

\* Deutsch, ch. Ges. Ber. 1877, 391. The rational formula of phthalylacetic acid,  $\text{C}_6\text{H}_4\text{C}(\text{CO})>\text{CH}-\text{COOH}$ , was based, not only on the properties of this compound, but also on the analogy it thus presented to the phthaleins of Baeyer. Lately, Baeyer has shown that the phthaleins are derivatives of triphenylmethane, and, therefore, by the dehydration that it is the carbonyl-oxygen atom ( $\text{C}=\text{O}$ ), and not the anhydride oxygen atom ( $\text{C}>\text{O}$ ) which enters into the formation of the eliminated molecule of water. This brings the formula of phthalylacetic acid again into question, which would have the rational formula,  $\text{C}_6\text{H}_4\text{C}(\text{CO})>\text{O}=\text{CH}-\text{COOH}$ , were the reaction in this case similar to that of the phthaleins. This new formula explains the behavior of the acid towards bases very satisfactorily, but the dibasic acid formed,  $\text{C}_6\text{H}_4\text{C}(\text{COOH})=\text{CH}-\text{COOH}$ , ought to possess properties, which would not be in accordance with those of the acid obtained. Not only are we at a loss to understand its remarkable instability towards heat and bases, but the compound obtained by the action of bromine upon it, which would have the rational formula,  $\text{C}_6\text{H}_4\text{C}(\text{COOH})\text{Br}-\text{CHBr}_2$ , yields, when decomposed by bases, bromoform and phthalic acid, whereas, according to the new rational formula, methylene bromide, phthalic and hydrobromic acid should have been obtained. There are other decompositions of phthalylacetic acid which would not be satisfactorily explained by the new formula, and it is, therefore, advisable to accept for the present the formula as originally proposed.

† Deutsch. ch. Ges. Ber. 1877, 1559, 2207; 1878, 1007, 1679.

dried at 100°, was analyzed with the following results: .2105 gr. of substance gave .7187 gr. of CO<sub>2</sub>, and .1309 gr. of H<sub>2</sub>O.

		Calculated for C <sub>14</sub> H <sub>12</sub> .	Found.
C	...	93.33	93.12
H	...	6.67	6.91

The compound, therefore, possesses the empirical formula of stilbene, and I found by a comparison of their properties, that they coincided with each other in every respect. The yield of stilbene according to this new method, is very satisfactory; I should judge from 50 to 60 per cent. of the theoretical, and the method may therefore be recommended for the preparation of this substance.

The formation of stilbene by the action of benzoic aldehyde on phenylacetic acid, is expressed by the following equation:  $\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5 - \text{CH}_2 - \text{COOH} = \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{C}_6\text{H}_5 + \text{CO}_2 + \text{H}_2\text{O}$ .

The above described reaction is not only a convenient method for the preparation of stilbene, but firstly, by varying the aromatic aldehyde; secondly, by taking substituted derivatives of phenylacetic acid; and thirdly, by taking substituted derivatives of both the aldehyde and acid, numerous substitution derivatives of stilbene in the benzene nucleus may be obtained; and it is, therefore, of considerable interest, since the usual methods of obtaining substitution products of aromatic hydrocarbons in the benzene nucleus are, to a great extent, unavailable for the preparation of stilbene derivatives.

I have hitherto only examined the action of sodium acetate on mixtures of cumin and salicylic aldehydes with phenylacetic acid, and have obtained results in accordance with those anticipated. Equal parts of cumin aldehyde and phenylacetic acid were well mixed with about one-third part of anhydrous sodium acetate, and the mixture heated in a closed glass tube for about 15 hours at 250°. Upon opening the tube it was found to contain a considerable quantity of carbonic acid, and its contents were extracted several times with warm water, then with dilute ammonia, and left a residue, which melted under warm water. This residue was treated, in alcoholic solution, repeatedly with animal charcoal, and finally crystallized three times from a hot solution of the same solvent.

The substance thus obtained crystallizes in fine, glittering

scales, which congregate in clusters that resemble cauliflower in their form. It is insoluble in cold and very slightly in warm water. In cold alcohol moderately, but very soluble in warm. It melts at 83–84°, and solidifies on cooling. The compound acts towards bromine as an unsaturated body, absorbing that reagent and forming a bromine additional product, which was not examined.

The substance, dried in vacuum, was analyzed: .1845 gr. of substance gave .6186 gr. of CO<sub>2</sub> and .1416 gr. of H<sub>2</sub>O.

		Calculated for C <sub>17</sub> H <sub>18</sub> .	Found.
C	...	91.89	91.47
H	...	8.11	8.53

The empirical formula C<sub>17</sub>H<sub>18</sub> is expressed rationally by C<sub>6</sub>H<sub>4</sub> $\frac{C_3H_7}{CH=CH}$ —C<sub>6</sub>H<sub>5</sub>, and the compound may therefore be called isopropylstilbene, its formation being according to the following equation: C<sub>6</sub>H<sub>4</sub> $\frac{C_3H_7}{CHO}$  + C<sub>6</sub>H<sub>5</sub>—CH<sub>2</sub>COOH = C<sub>6</sub>H<sub>4</sub> $\frac{C_3H_7}{CH=CH}$ —C<sub>6</sub>H<sub>5</sub> + CO<sub>2</sub> + H<sub>2</sub>O.

The behavior of a mixture of salicylic aldehyde and phenyl-acetic acid towards sodium acetate was examined under conditions similar to those employed in the synthesis of stilbene. Equal parts of the aldehyde and acid and about one-third part of anhydrous sodium acetate were well mixed, and the mixture heated in a closed tube for about 12 hours at 200°. Upon opening the tube carbonic acid was evolved, but I found that the reaction in this case was very complicated, it giving rise to a large quantity of resinous matter, from which a crystalline compound could only be obtained with considerable difficulty. Although the proportions of the ingredients of the mixture, as well as the temperature to which they were exposed, were considerably varied, I found that more satisfactory results were not obtained. The contents of the tube, treated as above, were first boiled with water, then with dilute ammonia, and the residue extracted several times with hot alcohol. The infusions were united, and the solution, after standing in an open vessel for some time, deposited a resinous mass. If, on the addition of water to a small quantity of the filtrate from this resinous mass, a crystalline precipitate was obtained, the whole filtrate was treated in a like manner; if,

however, the precipitate was of a resinous character, the solution was still allowed to evaporate by exposure to the air, and it deposited a further quantity of the amorphous matter. The addition of water to the alcoholic solution obtained by filtration, was always found to yield a crystalline precipitate, which consisted of small globular masses, and which, for further purification, were dissolved in alcohol, treated repeatedly with animal charcoal, and finally crystallized 4 or 5 times from the same solvent.

An analysis of the substance, dried at 100°, gave: .2182 gr. of substance gave .6849 gr. of CO<sub>2</sub> and .1251 gr. of H<sub>2</sub>O.

		Calculated for C <sub>14</sub> H <sub>12</sub> O.	Found.
C	...	85.72	85.60
H	...	6.12	6.37

The compound crystallizes from alcohol in long, colorless, arborescent needles, which melt at 135–136°, and solidify on cooling. It is insoluble in cold and almost insoluble in warm water. Cold alcohol dissolves it slightly, in warm alcohol it dissolves very readily. The yield of this compound is very small, owing to the large amount of resinous matter formed in the reaction.

Although this compound has not been sufficiently investigated to allow its rational formula to be given with any great degree of certainty, still the analogy which its formation presents to those of the preceding compounds, leads us to consider it as a derivative of stilbene, in which case the formula is expressed rationally by  $C_6H_4\overset{OH}{CH=CH}-C_6H_5$ , and the compound is ortho-oxystilbene, its formation being according to the equation:  $C_6H_4\overset{OH}{CHO} + C_6H_5CH_2COOH = C_6H_4\overset{OH}{CH=CH}C_6H_5 + CO_2 + H_2O$ .

I have, furthermore, made numerous experiments on the action of sodium acetate on a mixture of benzoic aldehyde and succinic acid, but without satisfactory results. The product formed was a greenish-yellow resin, from which a crystalline compound was only once obtained, which I will not describe, since all further experiments to ascertain the precise conditions under which it was formed were without result.

ON A NEW METHOD FOR THE SEPARATION AND  
SUBSEQUENT TREATMENT OF PRECIPITATES  
IN CHEMICAL ANALYSIS.\*

BY F. A. GOOCH.

The introduction of Bunsen's method of filtration and immediate ignition of precipitates in the moist condition has left little to be desired as regards accuracy of result and rapidity of execution, in the treatment of precipitates which may be submitted to high temperatures in contact with carbonaceous matter. In analytical methods which require that filter-paper and precipitate shall be ignited apart, or dried together at a temperature below the point at which paper begins to char, the same degree of exactness has not, in general, been hitherto attained.

To obviate the difficulty of bringing a paper-filter of ordinary dimensions, particularly when covered with a voluminous precipitate, to a definite condition of desiccation, the sand-filters of Dr. Gibbs and Taylor,† the porous cones of Munroe,‡ and finally the process of reverse filtering, first applied to quantitative work by Carmichael,§ improved by Casamajor,|| and thoroughly elaborated by Professor Cooke,¶ have been successively brought forward.

The latter process gives most excellent results in the separation of precipitates which settle quickly and completely; and, inasmuch as many precipitates which of themselves are not inclined to fall rapidly may be made to do so by proper treatment (by boiling, for example, the addition of ammonium salts, Chatard's\*\* method of granulating gelatinous precipitates, or other similar device), the field of usefulness of this process is wide.

The sand-filters in skilful hands, and the porous cones with no more than ordinary care, give accurate results, and possess

\* Presented to the American Academy of Arts and Sciences. Communicated by the Author.

† Am. Jour. [2], vol. xliv. p. 215.

§ Zeitschr. f. Chem. [N. F.], Bd. 6, p. 481.

¶ Proc. Am. Acad. Arts & Sci. vol. xii. p. 124.

‡ Am. Jour. [3], vol. i. p. 1.

|| Am. Chem. vol. v. p. 441.

\*\* Am. Jour. [2], vol. 1, p. 247.

moreover the advantage of being applicable to the filtration of liquids which quickly destroy woody fibre. The length of time required to dry them thoroughly, and their sensitiveness to atmospheric conditions, are their great drawbacks.

For the simple filtration of corrosive liquids without reference to a subsequent estimation of the precipitate, filters of sand, broken glass, garnets, and fibrous asbestos have for a time been used. More recently, asbestos has been moulded into the shape of an ordinary filter: in the dry state by Løwe,\* by rubbing between hollow and a solid wooden cones; in the wet state by Gruner,† by grinding asbestos, mixed in a mortar with water, to a pulp, transferring the mixture to a funnel choked with asbestos, inserting an accurately fitting cone of brass gauze, which presses the asbestos against the walls of the funnel, pouring off the water, carefully removing the cone and drying the layer of asbestos which adheres to the glass. Böttger‡ has used filters of gun-cotton; and Bunsen§ has devised a filtering apparatus for corrosive liquids to be attached to his pump, which consists of a disc of artificial pumice fitted to a conical tube and packed round its edge with fibrous asbestos.

None of these later-mentioned methods, however, are well adapted to the quantitative estimation of precipitates.

Impressed with the desirability of further improvement in those processes of quantitative analysis which involve the use of dried filters, or the separation of filter and precipitate before ignition, I have had the good fortune, in taking the matter up in turn, to succeed in devising and preparing a felt of anhydrous asbestos, which is capable of filtering liquids with a rapidity and efficiency at least as great as may be obtained by the use of good filter paper; is light, compact, incombustible at the highest temperatures used in analytical processes; is not acted upon by acids (excepting hydrofluoric acid) or alkalis; is sufficiently coherent to resist entirely the disintegrating action of a liquid forced through it under the pressure of the Bunsen pump, and which may moreover be prepared by a very simple process; in short, a filtering material which, in my belief, makes it possible to reach a high degree of accuracy

\* *Dingl. pol. Jour.* cxlviii. 444.

† *Dingl. pol. Jour.* clv. p. 463.

‡ *Jahresb. Chem.* 1869, p. 990.

§ *Ann. Ch. Pharm.* cxlviii. p. 290.

in many analytical processes which hitherto have been none of the best, and to add to those already known new methods which previously have been impracticable.

My mode of preparing and using the asbestos felt is as follows:—

*First*, white, silky, anhydrous asbestos,\* is scraped to a fine short down with an ordinary knife-blade, boiled with hydrochloric acid to remove traces of iron or other soluble matter, washed by decantation and set aside for use.

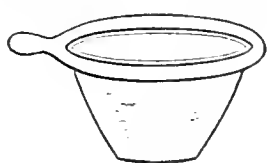


Fig. 1.

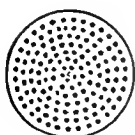


Fig. 2.

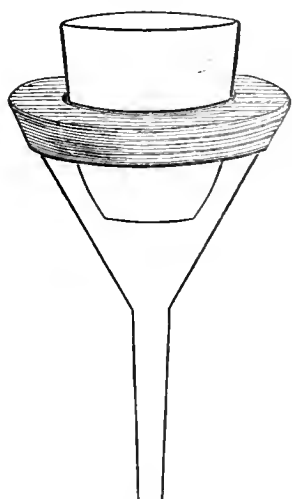


Fig. 3.

*Secondly*, a platinum crucible of ordinary size, preferably of the broad low pattern (Fig. 1), is chosen, and the bottom (Fig. 2) perforated with fine holes (the more numerous and the finer the better) by means of a steel point; or, better still, the bottom may be made of fine platinum gauze. Next, a Bunsen funnel of the proper size is selected, and—following Munroe's plan for holding his porous cones—over the top a short piece of rubber tubing is stretched and drawn down until the portion above the funnel† arranges itself at right angles to the direction of the stem. Within the opening in the rubber, the perforated crucible is fitted as shown in figure 3, and the funnel is connected with the receiver of a Bunsen pump or other exhausting apparatus in the ordinary manner.

To make the asbestos felt, the pressure of the pump is applied, and a little of the asbestos prepared as described, and suspended in water, is poured into the crucible. The rubber and the crucible are held together by the pressure of the vacuum-pump with sufficient force to make an air-tight joint; the water is drawn through, and the asbestos is deposited

\* Note, November 1879. I have found it very hard to procure asbestos of the proper quality from dealers in this country: but it would appear from the fact that several lots imported from Germany at different times have proved to be serviceable, and some of them excellent, that the difficulty is not due to a scantiness in the natural supply.

† Note, November 1879. It is better, as Professor H. B. Hill suggests, to leave a margin of the inner edge projecting upward.

almost instantly in a close compact layer upon the perforated bottom ; more asbestos (if necessary) in suspension as before being poured upon the first, until the layer becomes sufficiently thick for the purpose for which it is intended. Finally, a little distilled water is drawn through the apparatus to wash away any filaments that might cling to the under side, and the filter is ready for use : the whole process occupying less time than is necessary to fold and fit an ordinary paper-filter to a funnel.

To prepare the filter for the estimation of a precipitate, the crucible with the felt undisturbed is removed from the funnel and ignited. In case the precipitate, to be subsequently collected, must be heated to a very high temperature for a long time, it is better to enclose the perforated crucible with its felt within another crucible ; because, in such cases, asbestos felt is apt to curl at the edges, and without such precaution some of the precipitate might drop through the perforations and be lost. For drying at low temperatures, however, and even for ordinary ignitions, a second crucible is unnecessary ; but, during the ignition of an easily reducible substance, care must be taken to prevent the contact of unburnt gas with the perforated bottom.

To perform the filtration, the crucible is replaced in the funnel, the pressure applied, and the process conducted precisely as in an ordinary filtration by the Bunsen pump. It is necessary to observe that the vacuum-pump is to be started before pouring the liquid upon the filter. The final drying or ignition, as the case may be, of precipitate and filter is made without difficulty, or need of extra precaution.

When turbid liquids are to be filtered, or gelatinous precipitates to be separated, instead of the perforated crucible, I prefer to use a platinum cone (Figs. 4 and 5), the upper part of foil (to make a tight joint with the rubber fitting of the funnel), the lower of gauze. The method of covering the gauze with felt is identical with that described above. By reason of the larger filtering surface of this apparatus, the tendency to become

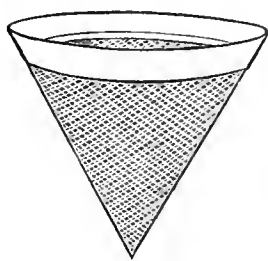


Fig. 4.

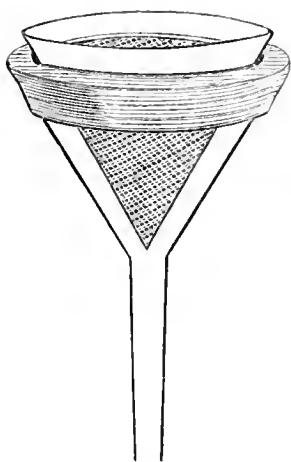


Fig. 5.

clogged is, of course, very much diminished. When subjected to prolonged ignition, the gauze cone is encircled within a crucible or a cone of platinum foil.

In operations in which platinum is liable to receive injury, a porcelain crucible, with a perforated bottom, may be used; but recourse to this is rarely necessary, particularly when one may use the gauze cone protected, as it is, by asbestos felt; moreover the perforation of porcelain with numerous fine holes is a matter of considerable difficulty and expense.

Asbestos felt may be also used in the process of reverse filtering, it being merely necessary to dip the platinum rose into the asbestos mixture, after starting the vacuum-pump, in order to make the felt. The rose, with the felt attached, and the vessel in which the precipitate is collected, are to be weighed together, both before and after filtration.

Nothing can be simpler than the whole method of preparation and use of the apparatus which I have described, and its efficiency is extremely great. Clean water may, under the pressure of a Bunsen pump, be passed through a gauze cone coated with asbestos felt, which exposes a filtering surface of twenty-four square centimetres (nearly the same as that of a paper filter eight centimetres in diameter, when folded in the ordinary manner), with ease at the rate of a litre per minute.

When the filtering surface is less, the rapidity of filtration is, of course, somewhat diminished, but, supposing the asbestos used to be of the best quality, always exceeds that of paper of the same dimensions. When the felt is deposited upon gauze, the layer may be surprisingly thin and yet be efficient enough for all ordinary purposes. If the layer of felt be quite thick, the filtrate from baric sulphate freshly precipitated in the cold, may be made to pass through clear. But the great superiority of asbestos felt lies in its constancy of weight, whether dried at high or low temperatures, the rapidity with which it may be safely and completely dried, and its refractoriness as regards acids (excepting hydrofluoric acid) and alkalis. These advantages appear most prominently in processes which involve the separation and desiccation:—

*First*, of precipitates which (like  $K_2PtCl_6$ ,  $[Hg_2]Cl_2$ ) must be dried at low temperatures, on account of a tendency to decompose spontaneously at high temperatures;

*Secondly*, of precipitates which (like  $Sb_2S_3$ ,  $PbSO_4$ ,  $ZnCO_3$ ) have usually been dried slowly and tediously at low temperatures, or have been separated from the filter before ignition, to avoid the danger of reduction by heating in contact with carbon;

*Thirdly*, of precipitates which (like  $(NH_4)_2Mg_2P_2O_8$ ,  $(NH_4)_2Mn_2P_2O_8$ ) may be ignited in contact with carbon, but which make its complete combustion difficult.

In all cases, the time required to dry or ignite precipitate and filter is a minimum, inasmuch as heat may be applied as soon and to as high a degree as the precipitate itself will permit. Even in processes in which paper filters find their most convenient application, paper has generally no superiority over asbestos felt.

To illustrate the cohesiveness and refractory nature of the felt, I append the account of a single experiment. All of the liquids used had been previously filtered, excepting the distilled water with which the filter was washed, after the passage of each liquid. This precaution was considered unnecessary in the case of the water; but, if it had been taken, the slight *increase* of weight which was observed during the experiment would probably have been prevented.

Weight, in grammes, of crucible and felt, after ignition	20.2020
after second ignition . . . . .	20.2020
after passing 100 cm <sup>3</sup> of strong HCl through the filter <i>ten</i> times, washing and igniting . . . .	20.2020
after passing 100 cm <sup>3</sup> of strong HNO <sub>3</sub> through the filter <i>ten</i> times, washing and igniting . . .	20.2021
after passing 100 cm <sup>3</sup> of strong H <sub>2</sub> SO <sub>4</sub> through the filter <i>five</i> times, washing and igniting . .	20.2022
after passing 100 cm <sup>3</sup> of a mixture of strong H <sub>2</sub> SO <sub>4</sub> and water in equal parts, <i>ten</i> times through the filter, washing and igniting . . . . .	20.2024
after passing 100 cm <sup>3</sup> of water, containing in solution 50 grammes of NaOH <i>ten</i> times through the filter, washing and igniting . . . . .	20.2028
Weight of crucible . . . . .	20.1932
“ “ felt . . . . .	.0088

The whole process, involving, in all, the filtration of five litres of liquid (of which one litre was viscous), more than forty changes of the receiver, together with the ignition, cooling, and weighing of the crucible and felt seven times, was completed in two hours and ten minutes. The disc of felt was eleven millimetres in diameter.

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## ON SEVERAL SPANISH MINERALS.

By F. A. GENTH, JR.

During spring of last year I had occasion to examine some minerals which had been presented to the University of Pennsylvania by the Spanish Government, at the close of the late Centennial Exhibition.

Among these were two of more than ordinary interest.

The first, which formed the principal portion of an ore, and was indicated in the Spanish catalogue as "*Sulfo-arseniuro de nikel*," from Benahanis, Province of Malaga, proved to be a cobaltiferous gersdorffite; the other, labelled "*Sulfuro de antimonio argentifero*," from the Province of Huelva, was found to be a massive variety of jamesonite.

### *Cobaltiferous Gersdorffite.*

The gangue-rock, in which the gersdorffite occurs, is calcite. This is found in large, white, crystalline, cleavable, masses, oftentimes so intimately mixed with the gersdorffite that they seem to be but one mineral of a light grey color. It then has a conchoidal fracture.

When placed in dilute hydrochloric acid the calcite dissolves, and the gersdorffite remains behind as a very fine crystalline powder, the particles of which are too small and indistinct for one to recognize any definite form. Granular massive.  $H = 5$ ; Sp. gr. = 5.856. Lustre metallic, but somewhat tarnished. Streak greyish-black. Color grey.

Before the blowpipe, in the closed tube, it gives a yellowish-brown sublimate of sulphide of arsenic, and sulphur above the same. In the open tube fumes of sulphurous oxide are given off, and a white crystalline sublimate of arsenious oxide is formed on the cold parts of the tube. On charcoal it is reduced to a white, bright, and brittle globule, with the emission of arsenical and sulphurous fumes.

Treated with successive portions of borax, the iron, cobalt, and nickel reactions are produced.

It is not acted upon by hydrochloric acid, but is decomposed by nitric acid, with the separation of sulphur and arsenious oxide. The solution is of a brownish green color.

An analysis of the gersdorffite, in which the cobalt was separated from the nickel by  $\text{KNO}_2$ , gave the following result:

S	...	22.01
As	...	39.71
Fe	...	1.12
Ni	...	24.83
Co	...	12.54
Cu	...	0.25
		<hr/>
		100.46

which corresponds with the formula  $\text{R}(\text{S}, \text{As})_2$  in which the Ni : Co as 2 : 1 and the S : As in the ratio of 14 : 11, which would make it a gersdorffite, very rich in cobalt.

Associated with the gersdorffite and calcite are,

(a) Chalcopyrite, mostly massive, often intimately mixed with the gersdorffite; generally tarnished.

(b) Erythrite, in beautiful, but very small rose colored crystals and crystalline scales, some showing a monoclinic form. The color is less blue than is generally the case, but a qualitative test gave only cobaltous oxide, arsenic pentoxide, and water.

(c) Pharmacolite, in globular botryoidal masses, of a pale reddish white, or flesh-red, color, due to the admixture of some arsenate of cobalt; structure radiating; lustre silky.

(d) Lavendulite, a beautiful, pale, ultra-marine-blue mineral, forming a very thin coating. Very rare; only one of the specimens shows a minute portion of lavendulite.

(e) Olivenite, (?) in globular aggregations of a deep green color; very probably olivenite, as it gave the reaction for copper.

(f) Aragonite, in white elongated needles and spear-shaped crystals, radiating from common centres, but too small and indistinct to determine their form. A qualitative test gave CaO and CO<sub>2</sub>.

*Jamesonite.*

The "Sulfuro de antimonio argentifero," from the Province of Huelva, is a mineral which is indistinctly crystalline, the particles showing lamination. Massive. Fracture uneven.  $H = 2.5$ . Sp. gr. = 5.467; soils paper. Lustre metallic. Color dark steel grey. Streak almost black. Opaque.

Before the blowpipe it fuses easily, giving a sublimate of sulphur and antimonious sulphide in the closed tube, and a white sublimate of antimonious oxide, and sulphurous oxide, in the open tube. On charcoal, with soda, it yields a metallic button of lead and antimony, surrounded by a white incrustation which is yellow nearer the assay.

Soluble in hydrochloric acid, with the evolution of hydrogen sulphide, and separation of plumbic chloride; in nitric acid with the separation of antimonious oxide, plumbic sulphate, and sulphur.

The mineral appeared to be homogeneous, with the exception that a considerable quantity of pyrite was disseminated throughout the entire mass, so that it was impossible to obtain material for analysis perfectly free from it.

There was also present a yellowish white soft mineral, with a waxy lustre, which was not further examined.

The analysis gave the following result:

Fe	...	5.95
Ag, Cu	...	0.28
Pb	...	38.29
* Sb	...	33.15
S	...	23.60
		<hr/>
		101.27

\* Sb = 122.

Another Sb determination gave 33.27 per cent.

This would give the formula  $(\text{Pb Fe})_2 \text{Sb}_2 \text{S}_5$ , together with a small quantity ( $\frac{1}{15}$ ) of pyrite. After deducting the pyrite, the pure mineral has the following composition:

Sb	...	34.03
S	...	22.31
Pb	...	38.49
Fe	...	5.16
		<hr/> 99.99

CHEMICAL LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA,  
WEST PHILADELPHIA, *November 14th, 1879.*

## A METHOD FOR ESTIMATING BISMUTH VOLUMETRICALLY.

BY M. KUHARA,

*Fellow in Chemistry, Johns Hopkins University.*

Bismuth may be estimated gravimetrically as  $2\text{BiAsO}_4 \cdot \text{H}_2\text{O}$  (dried at  $100^\circ$ – $120^\circ$ ), by precipitating its nitric acid solution with arsenic acid or sodic arseniate, collecting the precipitate on a weighed filter after washing it by decantation, and weighing the filter and precipitate together.\* In carrying out this process of estimation, however, various difficulties are met with.

It occurred to me that by taking advantage of Bøedeker's method for the estimation of arsenic acid† the gravimetric method above referred to might be converted into a volumetric. My hopes were completely realized, as the new method gives very accurate results.

The method was based upon the precipitation of bismuth, as  $\text{BiAsO}_4$ , from its nitric acid solution, by adding a measured

\*H. Salkowski, Jour. pr. Ch. 104, 170. Zeit. f. anal. Ch. 8, 205.

†Fresenius Quant. Analysis, p. 256.

quantity of standard solution of disodic arseniate in slight excess, and upon the determination of the amount of residual arseniate by means of standard uranic nitrate. In carrying out the estimation, the nitric acid solution of bismuth under examination must be free from hydrochloric acid, as well as substances precipitable by arseniate. Before entering upon the process of actual analysis, the amount of bismuth in a solution to be examined was approximately ascertained by the same method as that employed in the actual analysis.

Now a convenient quantity of the solution under examination was taken, a slight excess of disodic arseniate solution whose exact strength had been previously ascertained by a known weight of bismuth, was added to the solution, which was then agitated well without heating, and the mixture was set aside for a time to complete the reaction. The mixture containing the precipitate was rendered slightly alkaline with ammonia and then slightly acid with acetic acid. Now uranium solution, the relative strength of which as compared with that of arseniate had been previously ascertained, was allowed to run in from a burette very slowly, the mixture having been constantly well agitated to complete the reaction. The end of the reaction was recognized in the ordinary manner by means of ferrocyanide of potassium. From the amount of uranium solution used the excess of arseniate can be calculated; and from the actual amount of arseniate found by subtracting the excess from the whole amount taken, the quantity of bismuth can be easily calculated.

The following results were obtained:

For the standard solution of arseniate about 20.87 gr. of disodic arseniate were dissolved in 1 litre of water, and for the uranium solution about 35.6 gr. of uranic nitrate.

Relative strengths of arseniate and uranium solutions:—

		C. c. of arseniate taken.	C. c. of uranium solution used.
(1)	...	10	10.0
(2)	...	10	9.9
(3)	...	10	10.1
(4)	...	10	10.2
		—	—
			Mean = 10.06

1 c. c. of arseniate = 1.005 c. c. of uranium solution.

Standardization of arseniate in terms of bismuth :—

		Grams of bismuth taken.	C. c. of arseniate taken.	C. c. of uranium solution used.
(1)	...	.10	13	6.0
(2)	...	.10	13	5.9
(3)	...	.10	13	5.7
(4)	...	.10	13	5.7
(5)	...	.10	13	5.7

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Mean = 5.8

1 c. c. of arseniate = 0.01369 gr. of bismuth.

The following results were obtained by using a known weight of bismuth :—

		C.c. of Bi. taken.	C. c. of arseniate taken.	C. c. of uran. solution used.	C. c. of arseniate used.	Bismuth found.
(1)	...	.125	12	3.3	8.7	.119103
(2)	...	.125	12	3.2	8.8	.120472
(3)	...	.125	12	3.3	8.7	.119103
(4)	...	.125	12	3.3	8.7	.119103
(5)	...	.125	12	3.1	8.9	.121841
(6)	..	.125	12	3.0	9.0	.123210
(7)	...	.125	12	2.9	9.1	.124579
(8)	...	.125	12	2.9	9.1	.124579
(9)	...	.125	12	2.9	9.1	.124579
(10)	...	.125	12	3.0	8.7	.119130

These results were not quite satisfactory, so other experiments were made.

Uranic nitrate solutions of different strengths were prepared, and that containing 43.2 gr. of crystallized uranic nitrate in one litre of water was found to give the best results. The strength of the arseniate solution remained the same.

Relative strength of sodic arseniate and uranic nitrate.—

		C. c. of arseni- ate taken.	C. c. of uran. solu- tion used.
(1)	...	10	8.95
(2)	...	10	8.90
(3)	...	10	8.80

---

Mean = 8.88

1 c. c. of uranic solution = 1.126 c. c. of arseniate.

Standardization of arseniate in terms of bismuth by using uranic nitrate solutions of different strengths :—

		Grams bismuth taken.	C. c. of arsen. taken.	C. c. of uran. used.	C. c. of arsen. used.
(1)	...	.1	13	4.95	7.427
(2)	...	.1	13	5.10	7.258
(3)	...	.1	13	5.15	7.201
					Mean = 7.295

1 c. c. of arseniate = .0137 gr. of bismuth.

The following results were obtained by using known weights of bismuth :—

		Grams bismuth taken.	C. c. of arsen. taken.	C. c. of uran. used.	Excess of arsen. found.	C. c. of arsen. used.	Bismuth found.	Difference. Gain or loss.
(1)	..	.125	12	2.57	2.893	9.107	.124766	+ .000240
(2)	..	.125	12	2.60	2.927	9.073	.124300	+ .000700
(3)	..	.125	12	2.60	2.927	9.073	.124300	+ .000700
(4)	..	.125	12	2.55	2.871	9.129	.125067	— .000067
(5)	..	.125	12	2.56	2.882	9.118	.124916	+ .000084
(6)	..	.125	12	2.60	2.927	9.073	.124300	+ .000700

## NEW RESULTS IN ELECTROLYSIS.

BY EDGAR F. SMITH.

Succeeding the publication of a short article upon the electrolytic estimation of cadmium,\* the idea suggested itself that perhaps the rarer metals would disclose new facts as regarded their behavior toward the electric current. In short, I concluded to experiment upon a series of inorganic salts in this direction, with what result the following lines will show.

Beginning first with uranium, I gradually obtained results which were highly interesting; yielding among others a new method of estimating this element, and at the same time an excellent separation of it from the alkalies, alkaline earths, &c.

\*Am. Jour. Sciences & Arts, Jan. 1879.

A platinum crucible containing about 10 c. c. of water, having in solution .1000 gr. of impure uranic acetate, was connected with the zinc pole of a bichromate battery of two cells, (pint flasks), while to the carbon pole was attached a copper wire carrying a platinum spiral, which was immersed in the cold aqueous solution. Upon allowing the current to act for about one quarter of an hour, a slight iridescent coating was perceptible upon the crucible sides. Thinking that heat might be of avail, I placed the platinum receptacle upon a water bath and heated the contents of the latter to about  $60^{\circ}$ - $70^{\circ}$ C. Very soon the crucible sides became covered with a thin pale film, which gradually grew thicker, while the liquid slowly lost its yellow color. Finally, when the solution was colorless, I perceived a change in the yellow deposit; it was gradually assuming a black color. The action of the battery was continued until the entire yellow colored mass had changed to black. The crucible was now disconnected from the battery, the clear liquid decanted through a filter and tested for uranium, but not any detected.

The black deposit was hastily examined, but nothing definite learned in regard to its composition. Not more than one and a half hours were required to precipitate the uranium and convert it into the black colored deposit.

A second portion of uranium acetate was treated as just mentioned, and when I had fully convinced myself that the precipitation of uranium in this form was complete, I took steps to procuring the black deposit in larger quantities in order that I might be able to learn its true composition.

To the solutions with which I experimented I invariably added a little free acetic acid, in order that the yellow hydrated uranic oxide might not separate too rapidly, and thus become mixed with the black, and escape conversion into the latter. To render this certain, I always treated the black deposit with warm dilute acetic acid before allowing it to dry.

The coating upon the crucible appeared black in color, and adhered tenaciously to the sides. In all experiments the platinum vessel in which the deposition occurred was placed on a water bath, and the temperature previously mentioned carefully preserved. From solutions of about .1 gr. substance in 10 c. c.  $H_2O$  the precipitation is most rapid.

When a rather large quantity of material had been obtained, it was dried by standing over sulphuric acid several days, and then subjected to analysis.

*Analysis of Black Deposit.*

1. 1.2061 gr. substance were placed in a carefully weighed platinum boat = 2.3968 gr., and this then introduced into a perfectly dry combustion tube of Bohemian glass, to one end of which was attached a calcium chloride tube weighing 21.2554 gr. After strong ignition in a combustion furnace, with a stream of dry oxygen gas playing over the substance, the calcium chloride tube was detached and reweighed. Its weight now equalled 21.3906 gr., showing an increase of 0.0542 gr. due to water. The platinum boat was carefully removed from the tube and weighed a second time.

3.5470 gr.	represented the	$\text{U}_3\text{O}_4$ + boat.
2.3968 "	"	plat. boat alone.
<hr/>		
1.1502 "	"	$\text{U}_3\text{O}_4$

The first weight of boat + substance = 3.6029 gr.  
and this minus the boat +  $\text{U}_3\text{O}_4$  = 3.5470

---

 .0559 gr.

which represents loss sustained upon ignition. The slight difference between this loss and the actual increase of the calcium chloride tube may be attributed to error in weighing, or perhaps to a slight loss of oxygen suffered by the uranium protosquioxide.

The 1.1502 gr.  $\text{U}_3\text{O}_4$  contained 0.9765 gr. uranium, corresponding to 80.96 per cent. Ur. The increase in weight of the calcium chloride tube equalled .0542 gr. water, corresponding to 4.63 per cent.  $\text{H}_2\text{O}$ .

*Analysis of Black Deposit.*

2. The platinum boat + sub. dried over sulphuric	
acid as before weighed . . . . .	3.5141 gr.
Platinum boat — sub. = . . . . .	2.3968 gr.
	<hr/>
	1.1451 gr.

material for analysis. This, upon ignition in a combustion tube, as described in (1), gave the following result :

Wt. of CaCl <sub>2</sub> tube + H <sub>2</sub> O	21.3189 gr.
“ “ “ — “	21.2738 gr.
	<hr/>
	.0451 gr.

represent the H<sub>2</sub>O.

The platinum boat carefully removed and reweighed, gave, weight of boat + Ur<sub>3</sub>O<sub>4</sub> = 3.4645 gr., and 3.5141 (first weight of boat + sub.) minus 3.4645 = .0496 = weight of H<sub>2</sub>O.

The slight difference here again between the amount of water found by actual increase in the weight of the calcium chloride tube and that indicated by the loss in weight of the boat is, unquestionably, to be ascribed to the loss of oxygen on the part of the Ur<sub>3</sub>O<sub>4</sub>.

Now, .0451 gr. H<sub>2</sub>O = 4.05 per cent. H<sub>2</sub>O, and 3.4645 gr. (Ur<sub>3</sub>O<sub>4</sub> + boat) minus 2.3968 gr. (wt. of boat) = 1.0677 gr. Ur<sub>3</sub>O<sub>4</sub> = .9065 gr. uranium, corresponding to 81.13 per cent. Ur.

The result of analysis would then be 81.13 per cent. uranium, 4.05 per cent. water, and 14.82 per cent. oxygen, calculated from the weight of protosquinixide of uranium obtained.

Upon calculating with a view of arriving at the chemical formula of the oxide from the above analysis we get :

#### Analysis 1.

80.96 per cent. Ur	÷ 120 = 67	} ÷ 11 =	6	3
14.39 “ O	÷ 16 = 89		8	or 4
4.63 “ H <sub>2</sub> O	÷ 18 = 25		2	1

#### Analysis 2.

81.13 per cent. Ur	÷ 120 = 67	} ÷ 11 =	6	3
14.82 “ O	÷ 16 = 90		8	or 4
4.05 “ H <sub>2</sub> O	÷ 18 = 22		2	1

The numbers 3 : 4 : 1 would therefore represent the ratio in which the several constituents are present, or the black oxide as thrown out by the battery and as proven by analysis may be expressed by the formula Ur<sub>3</sub>O<sub>4</sub>H<sub>2</sub>O, which requires the following :

81.44	per cent.	uranium
4.07	“	water
14.49	“	oxygen

The black material never experienced any loss in weight by standing over sulphuric acid.

All the analyses which I have since made point to the above composition as being correct. When the dark deposit is dissolved in sulphuric acid, and potassium permanganate allowed to pass into the solution, a considerable quantity of uranous oxide was shown to be present. A number of qualitative tests confirmed this.

In some instances in the course of my work I noticed that the yellow hydrated sesquioxide remained on the crucible sides, and upon ignition, passed first into the anhydrous  $\text{U}_2\text{O}_3$ , then into  $\text{U}_3\text{O}_4$ . The occurrence of the sesquioxide will always be observed, unless the electric current is permitted to pass into the solution until the deposition on the crucible walls becomes thoroughly dark in color. Of course this precaution is not necessary when a simple determination of the uranium in solution is solely regarded.

To discover how reliable this method of precipitation would be, various salts were prepared and the uranium determined by this means.

#### *Double Acetate of Uranium and Sodium.*

The properties of this compound are sufficiently well known not to require a detailed description here. After obtaining it in the characteristic hemihedral form, (tetrahedrons), the crystals were reduced to a powder, carefully dried and analyzed with the following results:

1. 0.1575 gr. double acetate were dissolved in about 10 c. c. water in a platinum crucible. The latter was placed upon a water bath, the temperature of which was about  $70^\circ\text{C}$ , and the connections made with two cells of a potassium bichromate battery. In the course of two to three hours the uranium was completely thrown out of solution as protos sesquioxide, forming a black deposit upon the crucible sides. The crucible was now disconnected, the liquid filtered through a small filter, thus catching any loose particles of the oxide. After washing the deposit several times with hot water, the crucible and contents (the small filter having been added) were dried upon a warm plate and then ignited. Upon cooling the weight was taken. Found .0943 gr.  $\text{U}_3\text{O}_4$ , which equalled .08006 gr. uranium, corresponding to 50.83 per cent. Ur.

The filtrate and washings were evaporated and tested for uranium, but none was detected.

2. 0.1240 gr. material treated as just described above, gave .0743 gr.  $\text{Ur}_3\text{O}_4$ , corresponding to .0630 gr. uranium = 50.80 per cent. Ur. The time required for complete separation was the same as in (1).

3. 0.1461 gr. substance gave, after three hours' action of battery, .0815 gr.  $\text{Ur}_3\text{O}_4$ , equal to .07429 gr. uranium, corresponding to 50.84 per cent. Ur.

A combustion of the salt was then made to obtain the amount of carbon and hydrogen.

1. .2853 gr. dried double salt gave, upon burning with lead chromate in a stream of oxygen, .1640 gr.  $\text{CO}_2$  = 15.66 per cent. carbon and .0580 gr.  $\text{H}_2\text{O}$  = 2.26 per cent. hydrogen.

2. 0.2385 gr. substance treated as in (1) gave .1401 gr.  $\text{CO}_2$  = 16.00 per cent. carbon and .0490 gr.  $\text{H}_2\text{O}$  = 2.26 per cent. hydrogen.

These results show that this double salt is apparently a union of one molecule of uranium acetate with a like amount of sodium acetate. An examination of the theoretical and found percentages would indicate this:

$(\text{C}_2\text{H}_3\text{O}_2)_2\text{U}_2\text{O}_7$ ,  $\text{C}_2\text{H}_3\text{O}_2\text{Na}(\text{Ur} = 120)$ , requires:

			Found.	
50.84 per cent.	Ur	50.83	50.80	50.84
4.87	“ Na			
15.25	“ C	15.66	16.00	
1.90	“ H	2.24	2.26	
27.11	“ O			

#### *Double Acetate of Uranium and Potassium. Uranium Determination.*

1. 0.1090 gr. salt yielded .0610 gr.  $\text{Ur}_3\text{O}_4$ , which correspond to 47.43 per cent. uranium. The same dilution was observed here as in the case of the sodium and uranium acetate. Time, a little over two hours. The filtrate was free from uranium.

2. .2122 gr. double salt gave, after a little more than two hours, .1195 gr.  $\text{Ur}_3\text{O}_4$ , corresponding to 47.7 per cent. Ur.

A combustion of the salt gave the following:

0.8250 gr. salt carefully burned with lead chromate afforded .4192 gr. carbon dioxide, equalling .1143 gr. carbon, corresponding to 13.85 per cent. C; and .14099 gr.  $\text{H}_2\text{O}$  = .0156 gr. hydrogen or 1.87 per cent. H.

$(\text{C}_2\text{H}_3\text{O}_2)_2\text{U}_2\text{O}_2$ ,  $\text{C}_2\text{H}_3\text{O}_2\text{K} + 2\text{H}_2\text{O}$  requires :

		Found.
Carbon	14.22 per cent.	13.85 per cent.
Hydrogen	1.77 “	1.87 “
Uranium	47.42 “	47.43 — 47.7

The ratio of the acetates in this salt is also 1 : 1.

*Double Acetate of Uranium and Barium.*

This salt carefully prepared presents fine, shining, light yellow colored spangles. Only two determinations of the uranium by the battery were made, inasmuch as these were deemed sufficient to show that the method was perfectly applicable in such instances. In the first analysis the salt was not as pure as in (2); and this therefore would account for the low result in that instance.

1. 0.1090 gr. double salt gave .0528 gr.  $\text{U}_3\text{O}_8$ , corresponding to 41.11 per cent. uranium. Two hours were necessary for the deposition.

2. 0.1134 gr. salt gave .0556 gr.  $\text{U}_3\text{O}_8$ , equalling 41.63 per cent. uranium. About two hours were required for the complete separation of uranium oxide and its conversion into protos sesquioxide.

3. *Barium Estimation.* 0.1835 gr. salt gave .0384 gr.  $\text{BaSO}_4$  = .0225 gr. Ba, corresponding to 12.2 per cent. Ba.

The formula  $2(\text{C}_2\text{H}_3\text{O}_2)_2\text{U}_2\text{O}_2$ ;  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Ba} + 6\text{H}_2\text{O}$  requires :

		Found.
Uranium	41.99 per cent.	41.11 and 41.63 per cent.
Barium	11.98 “	12.20.

This method has also been employed in the analysis of certain silicates containing uranium, and afforded excellent results.\*

From the preceding analyses it will be seen that the method

\* This Journal, Vol. 1, No. 2, p. 88.

admits of a good separation of uranium from the alkalies and alkaline earths. The usual methods are more tedious and certainly not more accurate.

The method was extended to other salts of uranium with a view of ascertaining their behavior towards the electric current, and as they may perhaps be of interest, I append the results.

*Uranium Nitrate*, containing but five molecules of water, was first examined. 0.1200 gr. material dissolved in water in a small platinum crucible, and in the course of about three hours—the current being energetic—the precipitation was complete, and I obtained .0698 gr.  $\text{Ur}_3\text{O}_4$ , corresponding to .05926 gr. Ur or 49.38 per cent. Ur. The amount required theoretically 49.37 per cent. Ur. Free acid was not found in the solution.

I spent considerable time in endeavoring to throw out the protosesquioxide from a neutral solution of the chloride of uranium. The precipitation was indeed effected, only, however, after a number of hours, which of course rendered this salt useless for practical determinations. A constant liberation of chlorine gas was noticeable.

A neutral solution of the sulphate was experimented upon, but the precipitation proved to be very slow.

The double formate of uranium and sodium was made, and in aqueous solution subjected to the action of the battery. The uranium was thrown out as protosesquioxide as in the double acetates.

A solution of the double tartrate of uranium and sodium was evaporated, and permitted to stand for hours. Crystals were not formed, only a gelatinous mass remained. This salt was redissolved, and to the aqueous solution an excess of alcohol added, which caused the precipitation of the double tartrate as a light yellow-colored flocculent mass. After washing with alcohol the compound was dried and a weighed quantity dissolved in water. The aqueous solution was then brought in contact with the battery, but even at the expiration of two days' action of the electric current there was not any uranium precipitated.

The double citrate of uranium and sodium, prepared as the preceding salt and treated in a similar manner, gave like result. The salt is soluble in warm alcohol.

*Molybdenum.*

Molybdenum in the form of ammonium molybdate in aqueous solution was placed in a platinum crucible, and the latter connected with a two-celled bichromate battery (see Uranium). The current was allowed to act upon both cold and warm solutions. In a very short time a beautiful iridescence appeared upon the crucible walls, and as the action continued the deposit gradually became thicker and black in color. Just here I might add that if very dilute solutions of ammonium molybdate be treated in this way, an exceedingly thin and durable coating can be deposited upon metallic surfaces. Further investigation may perhaps render this of practical value.

I made several efforts to learn whether molybdenum could or could not be thrown out of solution — neutral or ammoniacal—completely by this method. One experiment in which 0.2000 gr. molybdic acid were dissolved in aqua ammonia, required for complete separation of the black deposit about one hundred hours. The liquid from the deposit, after the addition of nitric acid, was treated with sodium phosphate, but not the slightest trace of ammonio-phospho-molybdate was observed.

Ordinarily the black deposit appeared to form rapidly, but I soon observed that, after the coating had attained a certain thickness, the galvanic action almost ceased. Upon the addition of water to the solution, and thus exposing a fresh surface, the action was revived. This would indicate that the dark deposit was a poor conductor. Even when a large surface was exposed, the deposition, although complete, was so very slow that this method of determination was practically of little value.

The deposit was invariably washed very carefully with water and dried by exposure to the air. In acids it is very slowly soluble. The solution in hydrochloric acid diluted with water, possessed a brownish pink color. Ammonium hydrate precipitated from the same a brown mass. The deposit ignited in a closed crucible was converted into beautiful colorless leaflets of molybdic acid.

I prepared a rather large quantity of the black material and analyzed it, and found it to be the hydrate oxide.

*Water Determination.*

The air-dried substance was weighed in a platinum boat, and the latter then placed in a carefully dried Bohemian combustion tube, to one end of which a weighed calcium chloride tube was attached. Dry carbon dioxide was conducted through the same, and when the air had been expelled the tube was brought to low redness; the passage of carbon dioxide being continued until the end of the operation.

.1310 gr. air-dried material treated as just described, gave .0250 gr. water, corresponding to 19.08 per cent.  $H_2O$ .

The residue in the boat possessed a color very similar to potassium permanganate. It was then treated with strong nitric acid in a beaker, and gradually converted into molybdic acid, ammonium hydrate added, and the solution then brought to boiling. When the excess of ammonia had been expelled, a dilute solution of lead acetate was added in slight excess. The ebullition was continued until the precipitate became granular. This it did in a few moments. It was then allowed to subside, the supernatant liquid filtered, the precipitate slightly washed, dried and weighed.

1. .0903 gr. ignited material treated as just mentioned, gave .2766 gr. lead molybdate, corresponding to .0722 gr. Mo = 79.95 per cent.

2. .1161 gr. ignited substance gave .3643 gr. lead molybdate, equivalent to .0922 gr. molybdenum = 79.60 per cent. Mo.

These results approach very closely those required by molybdenum oxide, and this unquestionably is the composition of the black deposit.

$Mo_2O_3 \cdot 3H_2O$  requires 18.36 per cent.  $H_2O$ , and the analysis above gave 19.00 per cent. The ignited residue gave 79.95 per cent. and 79.60 per cent. molybdenum, and the anhydrous  $Mo_2O_3$  requires 79.96 per cent. Mo.

*Tungsten.*

Several salts of tungstic acid were prepared and studied. Ammonium tungstate (.1000 gr. to about 30 cc. of water) was placed in a platinum crucible, about which circled the wire from the zinc pole of a two-celled bichromate battery, while into the solution dipped a platinum spiral attached to the cop-

per wire leading from the carbon pole. There was a brisk evolution of gas, which continued for twelve hours, without any visible alteration of the tungstate solution. The same result attended the action upon a sodium tungstate solution. After boiling a portion of powdered sodium tungstate with acetic acid, and allowing the current to pass through the solution, the liquid at once acquired a deep blue color, and gradually a very thin blue deposit formed on the crucible walls. By prolonged action of the current this was in part altered to brown, and on exposure to the air the latter slowly passed back to blue. I never succeeded in getting enough material for analytical purposes, although these were really superfluons, the blue deposit being undoubtedly the  $W_2O_5$  oxide ordinarily found in the reduction of tungsten solutions, while the brown was probably  $W(OH)_4(?)$

#### *Vanadium.*

Employing a solution of ammonium vanadate and having the same battery connection as in tungsten, I noticed, after brief action of the current, that the originally colorless liquid became yellow and gradually blue or green-yellow. Not any other change was observed.

With vanadium chloride like results were got. There was always a strong evolution of chlorine.

With the sulphate (excess of acid having been removed) I obtained in time an exceedingly minute, dark brown colored deposit, scattered here and there upon the crucible. This was observed, too, when the sulphate solution was mixed with ammonium sulphate in excess.

#### *Didymium.*

Neutral sulphate solution did not give any result whatever. With an acetate solution a deposit was noticed upon the zinc pole. This occurred, too, when a nitrate solution was employed. The slight deposition gave reliable reactions for didymium.

#### *Cerium.*

Solutions of the nitrate, sulphate, acetate, and double nitrate of cerium and ammonium were experimented with, but the

results were unsatisfactory. With a solution of the chloride I had quite a large deposit upon the zinc pole of the battery, which was light yellow in color. There was always some chlorine liberated. The separated oxide acted as a non-conductor, and the precipitation was at the most exceedingly slow. In presence of didymium some of the latter was always co-precipitated. This method of separating cerium could never be of any practical value.

I hope to continue this work upon the behavior of various inorganic salts towards the electric current, as time may permit. The tendency to this field of investigation has induced me to publish the above at this moment.

LABORATORY OF THE UNIV. OF PENN., Nov. 21, 1879.

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## NITROSULPHOBENZOIC ACIDS AND SOME DERIVATIVES.\*

By EDWARD HART.

Certain distinctive properties have been recognized as belonging to each of the three classes of bi-substituted benzenes known as ortho, meta, and para respectively. Ortho compounds melt and boil at lower temperatures than meta and para. Meta compounds come next in this respect, and para highest. This distinction, though a marked one, is not without numerous exceptions. Besides this difference, we recognize certain others more or less general. As a rule, ortho compounds are easily soluble, meta less so, and para least of all. Further, ortho compounds when treated with a mixture of potassium bichromate and sulphuric acid, are either completely destroyed and converted into compounds belonging to other series, or they suffer no change whatever. This does not apply to oxyacids, however, as Remsen† has

\*From the Author's Thesis presented to the Johns Hopkins University for the degree of Ph. D.

†Liebig's *Annalen*, 178, 295.

shown. Probably exception should also be made of amido compounds, which are easily broken up. This last distinctive property of ortho compounds loses much of its value in view of the fact that other oxidizing agents, as, for example, nitric acid and potassium permanganate, do not act in this way, but oxidize all three classes in nearly the same manner.

The object of this investigation has been to determine as far as possible the influence of the position of the substituting groups upon the physical properties of substituted benzenes.

A very large number of bi-substituted benzenes have been prepared, and some of them carefully studied, but the only generalizations with regard to their physical properties that have yet been made are those mentioned at the beginning of this article. The tri-substituted benzenes offer a better field for such work, since here the possibilities of isomerism increase, and the comparison can be made to cover more ground. None of these have been studied with sufficient care for this purpose, and it seemed best to commence by preparing all possible isomers of such a series, fix the position of the substituting groups in each, and then carefully study and compare the compounds themselves and their like derivatives.

The nitrosulphobenzoic acids were chosen for this purpose, for which they have several advantages. (1) They appear to be very stable compounds, a matter of the greatest importance. (2) All three substituting groups are unlike, and therefore a larger number of isomers are possible (in this case 10, while, with all groups alike but 3, with two alike, 6, are possible). (3) They are bibasic acids, hence a larger number of similar derivatives can probably be prepared. (4) They can probably be easily prepared in large quantity if at all, and from a number of different sources, thus making it easier to fix accurately the position of the substituting groups.

Two nitrosulphobenzoic and three amidosulphobenzoic acids had been made before this investigation was undertaken. In none of these were the relative positions of more than two groups known. They had all been prepared in small quantity and not very carefully studied.

By treating metanitrobenzoic acid with fuming sulphuric acid at a temperature near the boiling point of the latter

Mulder\* obtained granular crystals of a new salt, which may have been the barium salt of a nitrosulphobenzoic acid, but which he did not examine further. By treating metasulphobenzoic acid with a mixture of fuming nitric and sulphuric acids, Limpricht and Uslar† obtained a nitrosulphobenzoic acid, and by reduction with ammonium sulphide the corresponding amido acid. Griess‡ treated metamidobenzoic acid with sulphuric acid, and obtained two amidosulphobenzoic acids.

Finally, by heating parasulphaminebenzoic acid with a mixture of nitric and sulphuric acids, Remsen§ obtained another of these nitrosulphobenzoic acids, and prepared and analyzed its barium salt. He further indicated a method by which the constitution of the acids then known might be determined, as follows: "Three isomeric nitrobenzoic acids are known, and their constitution is also understood. If it were now possible to introduce the sulpho group in these, compounds would be obtained of which two would be identical with the known nitrosulphobenzoic acids. The constitution of the latter could then be easily determined."

#### *Metanitroparasulphobenzoic Acid.*

This is the acid of Remsen, and was prepared according to his directions, except that I used parasulphobenzoic, and not parasulphaminebenzoic acid. Parasulphobenzoic acid was first prepared nearly according to Remsen's directions, from the mixture of toluene sulphoacids by oxidation with potassium bichromate and sulphuric acid. Afterwards I found it much simpler to use potassium permanganate as the oxidizing agent. The yield is in this case much larger, and the process requires much less time. The method adopted after several trials is as follows: 100 gr. toluene is dissolved in the smallest possible quantity of fuming sulphuric acid. The solution is diluted, neutralized with chalk filtered from the calcium sulphate and evaporated to a small bulk. 350 gr. potassium permanganate is dissolved in warm water and added to the solution of the calcium salts; the volume of liquid is then made up to about 5 litres by adding water, and the solution heated over the lamp or on the steam bath until it becomes colorless. The liquid is

\* Liebig's Annalen, 34, 302.

† Jour. fuer prak. Chemie, 113, 244.

‡ Liebig's Annalen, 106, 27.

§ Liebig's Annalen, 178, 288.

then filtered from the oxides of manganese and the filtrate supersaturated with hydrochloric acid; barium chloride is then added, which throws down the parasulphobenzoic acid as the acid barium salt. This is purified by crystallizing once from its solution in boiling water. 100 gr. toluene yield about 200 gr. of the acid barium salt.

From the acid barium salt of parasulphobenzoic acid, meta-nitroparasulphobenzoic acid is prepared by treating it with a mixture of equal parts by weight of fuming nitric and sulphuric acids. 20 gr. acid barium salt require 100 gr. of the mixed acids. The mixture is heated in an evaporating-dish over the lamp until the nitric acid is driven off, diluted, neutralized with barium carbonate, and the barium salt obtained from the filtrate by evaporation. The acid is obtained from the barium salt by exact precipitation of the barium with sulphuric acid.

$\text{SO}_3\text{H}$   
*Metanitroparasulphobenzoic acid*,  $\text{C}_6\text{H}_3\text{CO}_2\text{H} + 2\text{H}_2\text{O}$ , crystal-  
 $\text{NO}_2$

lizes from water, in which it is very soluble, in short, thick prisms. The acid is very slightly soluble in alcohol, and almost completely insoluble in ether, chloroform and carbon bisulphide. The hydrated acid melts at  $130^\circ$ – $131^\circ$ . As the acid blackened and appeared to decompose at a temperature insufficient to drive off all the water, the amount of this was determined by adding a weighed portion to a weighed portion of Iceland spar, and the calcium salt so obtained heated until all water was driven off. In this way .2096 gr. acid + an excess of Iceland spar lost .0715 gr.  $\text{H}_2\text{O} + \text{CO}_2$ . Theory requires .0725 gr.

#### *Barium Salt.*

$\text{C}_6\text{H}_3\text{SO}_3\text{NO}_2 \begin{matrix} \text{CO}_2 \searrow \\ \nearrow \end{matrix} \text{Ba} + 4\text{H}_2\text{O}$ . This is the salt described by Remsen,

the method of preparing which has already been described. The yield from 20 gr. acid barium salt of parasulphobenzoic acid was in one case 15 gr. I am satisfied, however, that it often largely exceeds this. Remsen gives the salt  $1\frac{1}{2}$  molecules  $\text{H}_2\text{O}$ . The difference is probably due to the fact that the salt analyzed by Remsen was dried over sulphuric acid, while

the figures here given are for the air-dried salt. Experiment shows that the salt loses water very slowly over sulphuric acid, and it seems probable that Remsen's salt was not perfectly dried before analysis. The salt loses a little less than 3 molecules of water over sulphuric acid at the ordinary temperature. It crystallizes in yellow needles which unite at the ends, forming concentric groups. They are moderately soluble in cold and easily in hot water.

I. .2915 gr. salt lost .0435 gr. at 200°, and gave .1497 gr. BaSO<sub>4</sub>.

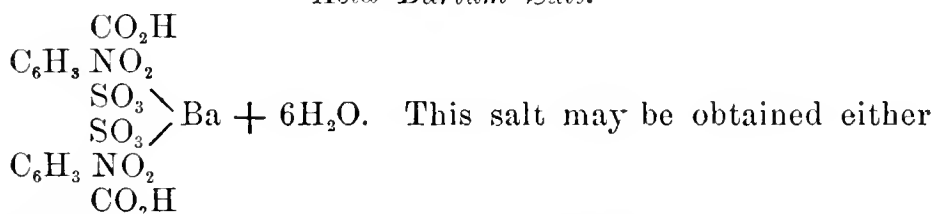
II. .2817 gr. salt lost .0318 gr. over sulphuric acid, and gave .1451 gr. BaSO<sub>4</sub>.

III. .3298 gr. salt lost .0382 gr. over sulphuric acid, and .0516 gr. at 235°.

Calculated.		Found.		
		I.	II.	III.
$\left. \begin{array}{l} \text{C}_6\text{H}_3 \text{ CO}_2 \\ \text{SO}_3 \\ \text{NO}_2 \end{array} \right\}$	245    53.96	...	...	...
Ba	137    30.18	30.00	30.28	...
4H <sub>2</sub> O	72    15.86	15.68	...	15.65
	<hr/> 454    100.00			
3H <sub>2</sub> O	<hr/> 12.39	...	11.28	11.59

In the mother liquor from this salt a very soluble yellow salt is contained. The manganese salt of this acid, as well as the zinc salt, appears to crystallize tolerably well, though they are both quite soluble. The entire amount on hand was lost, however, by a mishap before a pure salt had been obtained from it. From an analysis of the impure manganese salt, the acid appears to be dinitrosulphobenzoic, though this is as yet by no means certain.

#### *Acid Barium Salt.*



by treating a solution of the neutral salt with hydrochloric

acid, evaporating to crystallization, and recrystallizing the product, or by dividing a solution of the neutral salt in two equal portions; exactly precipitating the barium in one portion by sulphuric acid, and adding the other to it. It crystallizes in long prismatic needles, which attain great length under favorable circumstances. The crystals are nearly white. They are easily soluble in water—more soluble than the neutral salt. Solutions of the salt show a very marked tendency to creep up the sides of containing vessels. The salt loses three molecules of water over sulphuric acid.

I. .2104 gr. salt lost .0152 gr. over sulphuric acid, .0297 gr. at 180°, and gave .0669 gr. BaSO<sub>4</sub>.

II. .3758 gr. salt lost .0554 gr. at 210°, and gave .1209 gr. BaSO<sub>4</sub>.

III. .2481 gr. salt lost .0190 gr. over sulphuric acid, and .0357 gr. at 210°, and gave .0465 gr. BaSO<sub>4</sub>.

Calculated.			Found.		
			I.	II.	III.
$\left\{ \begin{array}{l} \text{C}_6\text{H}_3 \\ \text{CO}_2\text{H} \\ \text{NO}_2 \\ \text{SO}_3 \end{array} \right\}_2$	492	66.76	...	...	...
Ba	137	18.59	18.68	18.91	18.72
6H <sub>2</sub> O	108	14.65	14.12	14.72	14.39
	<hr/> 737	<hr/> 100.00			
3H <sub>2</sub> O		7.31	7.22	...	7.65

#### Copper Salt.

$\text{C}_6\text{H}_3 \begin{array}{l} \text{CO}_2 \\ \text{SO}_3 \\ \text{NO}_2 \end{array} \rangle \text{Cu} + 5\text{H}_2\text{O}$ . This salt forms small, hard, bluish-

green crystals. It was obtained by evaporating a solution of the salt over sulphuric acid. The salt is difficult to obtain in the pure state, as the solutions deposit a greenish-white substance when evaporated, which appears to be a basic salt. The salt loses two molecules of water over sulphuric acid, and the remainder at a higher temperature.

I. .1945 gr. salt lost .0208 gr. over sulphuric acid.

II. .1285 gr. salt lost .0269 gr. at 250° and gave .0205 gr. Cu.

Calculated.		Found.	
		I.	II.
$\left. \begin{array}{c} \text{CO}_2 \\ \text{C}_6\text{H}_3 \text{ SO}_3 \\ \text{NO}_2 \end{array} \right\}$	245      61.50	...	...
Cu	63.4      15.91		15.95
5H <sub>2</sub> O	90.      22.59	...	20.93
	<hr/> 398.4      100.00		
2H <sub>2</sub> O		10.69	...
		<hr/> 10.45	

The result for 5H<sub>2</sub>O agrees very poorly with the calculated percentage. Inasmuch as the solution was allowed to evaporate over sulphuric acid, and the amount of salt obtained was small, it may have lost a portion of its water. No. I, which represented much the purer portion of the salt obtained, was unfortunately lost before the analysis was completed. The study of the salt was laid by to make room for more important work, and will be again taken up hereafter.

#### Potassium Salt.

This salt forms small, hard prisms, very soluble in water. No analysis has yet been made.

#### Acid Potassium Salt.

$\text{CO}_2\text{H}$   
 $\text{C}_6\text{H}_3 \text{ SO}_3\text{K} + 1\frac{1}{2}\text{H}_2\text{O}$ . The salt was obtained by treating a  
 $\text{NO}_2$

concentrated solution of the neutral salt with hydrochloric acid and recrystallizing the product. It crystallizes in long silky needles, which are moderately soluble in water. On being exposed to the air on filter paper, these crystals break up into granular pieces before they are completely dry. The salt may also be obtained in six-sided plates by allowing a saturated solution to evaporate slowly. The analyses given below were made of the air-dried needles.

I. .2196 gr. salt lost .0191 gr. at 190°, and gave .0611 gr. K<sub>2</sub>SO<sub>4</sub>.

II. .1826 gr. salt lost .0163 gr., and gave .0503 gr. K<sub>2</sub>SO<sub>4</sub>.

	Calculated.		Found.	
	I.	II.	I.	II.
$\left. \begin{array}{c} \text{CO}_2\text{H} \\ \text{C}_6\text{H}_3\text{SO}_3 \\ \text{NO}_2 \end{array} \right\}$	246	78.82	...	...
K	39.1	12.53	12.49	12.37
$1\frac{1}{2}\text{H}_2\text{O}$	27.0	8.65	8.70	8.92
	<hr/> 312.1	<hr/> 100.00		

*Calcium Salt.*

$\left. \begin{array}{c} \text{CO}_2 \\ \text{C}_6\text{H}_3\text{SO}_3 \\ \text{NO}_2 \end{array} \right\} \text{Ca} + 5\text{H}_2\text{O}.$  The salt forms large prismatic

crystals of a slightly yellowish color, which are tolerably soluble in water. The crystals rapidly effloresce and fall to powder when exposed to the air.

I. .2362 gr. crystallized salt dried rapidly between filtering paper and weighed, lost .0336 gr. over sulphuric acid, and .0207 gr. additional at  $250^\circ$  and gave .0863 gr.  $\text{CaSO}_4$ .

II. .1998 gr. dried over sulphuric acid lost .0234 gr. at  $290^\circ$  and gave .0846 gr.  $\text{CaSO}_4$ .

	Calculated.		Found.	
	I.	II.	I.	II.
$\left. \begin{array}{c} \text{CO}_2 \\ \text{C}_6\text{H}_3\text{SO}_3 \\ \text{NO}_2 \end{array} \right\}$	245	65.33	...	...
Ca	40	10.67	10.74	...
$5\text{H}_2\text{O}$	90	24.00	22.99	...
	<hr/> 375	<hr/> 100.00	<hr/>	<hr/>
$\left\{ \begin{array}{l} 2\text{H}_2\text{O} \\ \text{Ca} \end{array} \right.$		11.21	10.21	11.71
		12.46	12.52	12.45

*Silver Salt.*

No analysis of this salt has yet been made. It is easily soluble in water and crystallizes in large prisms of a yellowish color.

*Metamidoparasulphobenzoic Acid.*

This is obtained by treating the potassium or ammonium-salt of the preceding acid with ammonium sulphide in excess,

and evaporating the solution on the water bath until the fumes given off no longer blacken lead paper; upon filtering off the sulphur which has separated, and adding hydrochloric acid, the acid mixed with sulphur is precipitated. It may be purified by converting it into the barium salt, filtering through animal chareoal to remove coloring matter, and reprecipitating with hydrochloric acid. The acid forms a white powder, which, when precipitated from a hot, not too concentrated solution, takes the form of warty masses with a slight tendency to crystallize. It is difficultly soluble even in boiling water, almost entirely insoluble in alcohol, ether and carbon bisulphide. When heated on platinum foil it blackens without previously melting, and gives off fumes with the odor of sulphur dioxide. The watery solution of the acid shows no fluorescence.

*Barium Salt.*

$\text{C}_6\text{H}_3\text{SO}_3\text{NH}_2 \begin{matrix} \text{CO}_2 \searrow \\ \nearrow \end{matrix} \text{Ba} + 3\text{H}_2\text{O}$ . Obtained by treating the acid with

water and barium carbonate. It crystallizes in well formed, sharply pointed crystals, which have a very beautiful lustre. A solution of the salt slowly decomposes when evaporated, or even if allowed to stand for a long time, becoming dirty brown or yellow. If such a solution be allowed to crystallize, the crystals are almost black. By filtering through a long tube containing animal chareoal, the coloring matter of such solutions may be removed, and the solutions then show a marked blue fluorescence. This fluorescence is less marked than in the case of another acid and its barium salt, to be presently described.

I. .1712 gr. salt lost .0232 gr. and gave .0953 gr.  $\text{BaSO}_4$ .

II. .2200 gr. salt lost .0296 gr. and gave .1252 gr.  $\text{BaSO}_4$ .

Calculated.		Found,	
		I.	II.
$\text{C}_6\text{H}_3\text{SO}_3\text{NH}_2 \begin{matrix} \text{CO}_2 \searrow \\ \nearrow \end{matrix}$	215	...	...
Ba	137	32.73	33.46
$3\text{H}_2\text{O}$	54	13.55	13.45
	<hr/> 406		
	100.00		

No. I. was made with a specimen of the salt which had considerable color and which was prepared before the proper method for purification was discovered. No. II. was made with white and quite pure salt.

This acid seems to be identical with one of those made by Griess. I have made the acid of Griess according to his method, and have no doubt that the two are identical, though no analyses have yet been made to test the matter thoroughly. These two methods of preparation—on the one hand from parasulphobenzoic acid, and on the other hand from metamido-benzoic acid—are sufficient proof that the name metamido-parasulphobenzoic acid correctly indicates its constitution. This proof is supported by another, to be considered hereafter.

*Paranitroorthosulphobenzoic Acid.*

In a preliminary notice\* it was stated that by treating paranitrotoluene with sulphuric acid and neutralizing with chalk, two calcium salts had been obtained, one containing 4, the second 6 molecules of water of crystallization, and which were believed to be the salts of two isomeric acids. A more careful study has, however, led to the conclusion that the first assumption was a mistaken one, and that the two salts differ only in the amounts of water of crystallization which they contain. When treated with phosphorous pentachloride and afterwards with ammonia, they are converted into amides of similar appearance, and melting at precisely the same temperature, 189°. Further, they both yield upon oxidation the same acid—paranitroorthosulphobenzoic. In this connection it may be noticed that Schwanert† has obtained a calcium salt of this acid containing but one molecule of water of crystallization. The proof for the constitution of the above toluene-nitrosulphonic acid was given by Ascher.‡ He converted the nitro into an amido acid, replaced the  $\text{NH}_2$  group by H by means of Griess's reaction, and by fusing the resulting toluene-sulphonic acid with potassium hydroxide obtained salicylic acid, thus showing that the sulpho group occupies the ortho position.

\* Ber. der deut. chem. Gesell. X. 1046.

† Liebig's Annalen, 186, 850.

‡ Liebig's Annalen, 161, 1, and Ber. der deut. chem. Gesell. IV. 649.

The potassium salt of the new acid was obtained from the above tolueneparanitroorthosulphonic acid by the oxidation of the calcium salt with potassium permanganate. Paranitrotoluene was dissolved in fuming sulphuric acid. The solution was gently heated and allowed to stand in a warm place, until on diluting with water a clear solution was obtained. The mixture was then diluted, neutralized with chalk, filtered from the calcium sulphate and excess of chalk, evaporated to a small bulk, and to the solution heated upon a water-bath potassium permanganate was added in small quantities at a time, until the solution was not decolorized after 4 or 5 hours' heating. The excess of permanganate was then destroyed by a little alcohol, and the filtrate from the oxides of manganese evaporated until the neutral potassium salt of the new acid crystallized out.

*Neutral Potassium Salt.*

$\text{CO}_2\text{K}$   
 $\text{C}_6\text{H}_3\text{SO}_3\text{K}$ . Obtained as above described. The salt is anhy-  
 $\text{NO}_2$

drous and crystallizes in groups of short, thick, opaque prisms, which mostly have a faint yellow color. They are tolerably soluble in cold and more easily in boiling water. The appearance of the crystals is very characteristic.

I. .2698 gr. salt gave .1444 gr  $\text{K}_2\text{SO}_4 = 24.02$  per cent. K.

II. .2733 gr. salt gave .1461 gr.  $\text{K}_2\text{SO}_4 = 24.00$  per cent.

K. Theory requires 24.19 per cent. K.

A determination of the sulphur by the method of Fahlberg and Iles, which Dr. Fahlberg kindly made, gave: .31225 gr. salt gave .2125 gr.  $\text{BaSO}_4 = 9.35$  per cent. S. Theory requires 9.46 per cent. S.

*Acid Potassium Salt.*

$\text{CO}_2\text{H}$   
 $\text{C}_6\text{H}_3\text{SO}_3\text{K} + \text{H}_2\text{O}$ . The salt was prepared by adding hydro-  
 $\text{NO}_2$

chloric acid to a concentrated cold solution of the neutral salt. It crystallizes in long, fine white needles, which are only moderately soluble in cold water. By slow evaporation of a saturated solution it may be obtained in thick, short, transparent prisms. The needles were analyzed with the following

result: .2339 gr. salt lost nothing over sulphuric acid; .0146 gr. at 150°, and gave .0662 gr. K<sub>2</sub>SO<sub>4</sub>.

Calculated.			Found.
$\left. \begin{array}{c} \text{CO}_2\text{H} \\ \text{C}_6\text{H}_3\text{SO}_3 \\ \text{NO}_2 \end{array} \right\}$	246	81.16	...
K	39.1	12.90	12.71
H <sub>2</sub> O	18	5.94	6.24
	<hr/> 303.1	<hr/> 100.00	

*Barium Salt.*

$\left. \begin{array}{c} \text{CO}_2 \\ \text{C}_6\text{H}_2\text{SO}_3 \\ \text{NO}_2 \end{array} \right\} \text{Ba.}$  Very insoluble, small, compact crystals ob-

tained by adding barium chloride to a hot, not too concentrated, solution of the potassium salt. If a saturated solution of the salt be evaporated over the free flame, it separates in very delicate mica-like plates with a beautiful pearly lustre. These plates when air-dried contain about 4 per cent. of water, which they lose in part at low temperatures. All the water, however, is not driven off until a temperature of over 200° is reached. The compact salt also contains water, but in smaller amount (about 3 per cent.) It seems probable therefore that the salt is anhydrous, but very hygroscopic.

I. .1539 gr. salt dried at 220° gave .0941 gr. BaSO<sub>4</sub> = 35.95 per cent. Ba.

II. .1259 gr. salt dried at 250° gave .0775 gr. BaSO<sub>4</sub> = 36.19 per cent Ba.

III. .2726 gr. salt dried at 250° gave .1653 gr. BaSO<sub>4</sub> = 35.66 per cent. Ba. Theory requires 35.85 per cent. Ba.

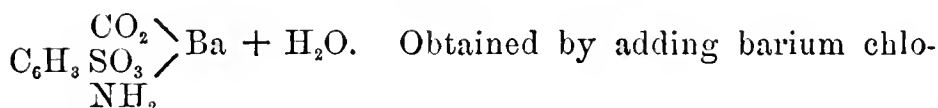
The copper and calcium salts of paranitroorthosulphobenzoic acid have been prepared, but as yet only in small quantities, and no analyses have been made. The copper salt is very soluble and crystallizes in fine blue needles. The calcium salt is also easily soluble and crystallizes in prisms.

*Paramidoorthosulphobenzoic Acid.*

Made by treating the potassium salt of the above acid with ammonium sulphide, evaporating to dryness on the

water bath, and adding hydrochloric acid to the filtered solution. The acid forms long, delicate needles, which are very slightly soluble in cold, more easily in boiling water; almost entirely insoluble in alcohol and ether. Solutions of the acid when evaporated do not become colored. If the solution be made neutral or alkaline, however, decomposition commences if the solution is kept hot, and soon becomes of a dirty brown or black color.

*Barium Salt.*



ride to a solution of the ammonium salt. Very fine needles, which unite to form groups. When a solution of the salt is rapidly evaporated, it separates in mica-like plates with a pearly lustre. The salt is difficultly soluble in water.

I. .1919 gr. salt lost .0100 gr. and gave .1201 gr.  $\text{BaSO}_4 = 5.21$  per cent.  $\text{H}_2\text{O}$  and 36.80 per cent. Ba.

II. .1742 gr. salt dried at  $220^\circ$  gave .1156  $\text{BaSO}_4 = 39.02$  per cent. Ba. Theory requires, for the hydrated salt, 4.87 per cent.  $\text{H}_2\text{O}$  and 37.03 per cent. Ba; for the dried salt, 38.92 per cent. Ba.

*Orthonitroparasulphobenzoic Acid.*

This acid was made by treating orthonitrotoluene with fuming sulphuric acid, neutralizing with chalk, evaporating the filtrate to a small bulk, and oxidizing the product by addition of potassium permanganate in small quantities at a time. The solution is filtered from oxides of manganese, neutralized with hydrochloric acid, and evaporated to a small bulk. Hydrochloric acid is then added in excess, which precipitates the acid potassium salt, which is easily purified by recrystallization.

*Potassium Salt*

Is very soluble in water, by which it is readily distinguished from the corresponding salt of paranitroorthosulphobenzoic acid. No analysis was made.

*Acid Potassium Salt.*

$\text{CO}_2\text{H}$   
 $\text{C}_6\text{H}_3\text{SO}_3\text{K}$  Anhydrous prismatic plates, which are tolerably  
 $\text{NO}_2$   
soluble in hot, less in cold water. .1980 gr. salt gave .0599 gr.  
 $\text{K}_2\text{SO}_4 = 13.58$  per cent. K. Theory requires 13.71 per  
cent. K.

*Barium Salt.*

$\text{CO}_2\text{H}$   
 $\text{C}_6\text{H}_3\text{SO}_3\text{Ba}$  +  $2\text{H}_2\text{O}$ . This is obtained from the neutral  
 $\text{NO}_2$   
potassium salt by adding barium chloride to a strong solution.  
The salt forms small granular crystals of a yellowish color,  
which are difficultly soluble in cold, more easily in boiling  
water.

.2199 gr. salt gave .0202 gr.  $\text{H}_2\text{O} = 9.19$  per cent., and .1204  
gr.  $\text{BaSO}_4$  which gives for the dried salt 35.45 per cent. Ba.  
Theory requires 8.61 per cent.  $\text{H}_2\text{O}$  and 35.86 per cent. Ba.

These results, though not as accurate as could be wished,  
when taken in connection with the analysis of the acid potas-  
sium salt sufficiently indicate the composition of the acid.  
The barium salt was prepared in small quantity, and was not  
as pure as was desirable. Another analysis will be made  
when larger quantities have been prepared.

The proof for the constitution of this acid is as follows:  
The toluenenitrosulphonic acid, from which it is derived by  
oxidation, was obtained by Beilstein and Kuhlberg\* by the  
action of fuming sulphuric acid upon orthonitrotoluene (called  
metanitrotoluene by B. and K., as salicylic acid was at that  
time supposed to be a meta compound). The same acid was  
likewise obtained by Engelhardt† by treating his  $\alpha$ -toluene-  
sulphonic acid with nitric acid. Anna Wolkow‡ has shown  
that the  $\alpha$ -acid of Engelhardt is tolueneparasulphonic acid,  
and she has also made the tolueneorthonitroparasulphonic  
acid from it by treating it with fuming nitric acid.

*Orthoamidoparasulphobenzoic Acid.*

Made from the nitro acid by treating the potassium salt  
with ammonium sulphide. The acid is precipitated from a

\* Liebig's Annalen, 155, 8.

† Ibid. 155, 19.

‡ Zeit. f. Chemie, 1870, 324.

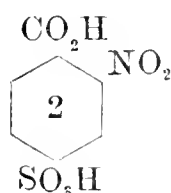
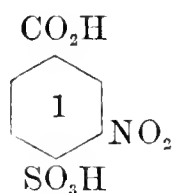
concentrated solution of its salts on adding hydrochloric acid. It crystallizes in beautiful rhombic plates of a yellowish color, and is tolerably soluble in hot water, slightly in cold water and in alcohol; almost entirely insoluble in ether and chloroform. Dilute solutions of the acid and its barium salt show a beautiful blue fluorescence. An estimation of the sulphur gave the following result:

.1951 gr. acid gave .2072  $\text{BaSO}_4 = 14.59$  per cent. S. Theory requires 14.70 per cent. S.

The barium salt of this acid has been prepared in small quantity, but no analysis has yet been made. The salt is white, dissolves tolerably easily in hot water, and separates in small crystals which unite to form groups. The salt easily decomposes in solution when evaporated.

In speaking of metamidoparasulphobenzoic acid it was stated that in addition to the proof there given, another consideration led to the same result. This second proof is found in connection with the above orthonitroparasulphobenzoic acid.

According to accepted ideas, but two nitroparasulphobenzoic acids are possible which would have the following formulæ:



Of these, according to the method of its formation, we must accept 2 as the correct formula for the acid last described. This leaves 1 as the only possibility for the other acid, and leads to the same result as the method of proof already given under the latter acid. A comparison of the acid first obtained by Remsen and the one made from orthonitrotoluene, as well as of their salts, given below, shows that they are entirely different.

*Metanitroparasulphobenzoic acid* contains  $2\text{H}_2\text{O}$  and melts at  $130^\circ\text{--}131^\circ$  easily soluble.

Potassium salt; small hard prisms, easily soluble in water.

*Orthonitroparasulphobenzoic acid* contains no water of crystallization.

Potassium salt; very soluble in water.

Acid potassium salt contains  $1\frac{1}{2}\text{H}_2\text{O}$ .

Barium salt contains  $4\text{H}_2\text{O}$ . Tolerably soluble. Loses  $3\text{H}_2\text{O}$  over  $\text{H}_2\text{SO}_4$ .

Amido-acid; white powder, very insoluble, no fluorescence.

Barium salt contains  $3\text{H}_2\text{O}$ .

Acid potassium salt is anhydrous.

Barium salt is anhydrous. Very slightly soluble.

Amido-acid; rhombic crystals, quite soluble, strong fluorescence.

Barium salt contains no water.

The work so far done may be summed up in the statement that two new nitrosulphobenzoic acids have been made, and their structure, as well as that of Remsen's acid, determined. The corresponding amido acids have also been prepared and so far examined that there will be no difficulty in recognizing them, should they again be met with. The acid of Limpriht and Uslar, and the second acid of Griess, have also been prepared in quantity. They are different from any of those examined. As soon as time offers, an attempt will be made to fix the position of the substituting groups. The number of nitro or amido acids now known, which differ from one another, is five. Other possible sources of nitrosulphobenzoic acids are as follows: (1) Action of nitric acid upon orthosulphobenzoic acid.\* (2) Of sulphuric acid upon orthonitrobenzoic acid. I have attempted to introduce the sulpho group into metanitro and paranitro benzoic acids in many ways, but entirely without success. (3) Action of sulphuric acid upon ortho and paramido benzoic acids. In the case of paramido benzoic acid the experiment has already been tried by Michael and Norton,† who obtained, not an amidosulphobenzoic acid, but one having the formula  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{SO}_6$ . (4) Action of sulphuric acid upon metanitrotoluene and oxidation of the product. (5) It may be that by treating the two nitro-ethylbenzenes with sulphuric acid, positions will be taken by the sulpho-group different from those in the nitrotoluenes.

After all possible ways have been tried, a thorough study of

\*Since the above was written an acid which appears to be new has been prepared in this way. The barium salt contains  $3\text{H}_2\text{O}$ , which it loses completely over sulphuric acid.

†Ber. der deut. chem. Gesell. 10, 580.

the salts, ethers, &c., of the isomeric acids will be made. It is proposed to compare 1st, melting points; 2d, solubility; 3d, crystalline form, especially of anhydrous compounds; 4th, number of molecules of water in isomeric salts.

This investigation was undertaken at the instigation of Professor Remsen, and most of the work was done in his laboratory.

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## REVIEWS AND REPORTS.

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### BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

*(Continued from page 284.)*

#### HEAVY CHEMICAL MANUFACTURES — *Continued.*

##### *Salts.*

*Nitre.*—An important addition to our knowledge on the much examined but still obscure subject of nitrification has been lately made by the researches of Mueller, Schloesing, Muentz, Warington and Storer, in reference to the influence of a living ferment in producing this peculiar form of chemical change in nitrogenous material. At the same time new observations have been made upon the range of temperature within which nitrification takes place, upon the unfavorable influence of light, the importance of the presence of calcium carbonate or equivalent basic material, the circumstances under which a nitrite rather than a nitrate is produced, &c. These observations and experimental results will undoubtedly admit of useful application whenever the manufacture of nitre in the so-called "beds" has to be resorted to. Some of the facts recorded by Warington in regard to the influence of light and temperature are quite in accord with results afforded on a larger scale by nitre beds established in the Southern States during the war of 1861–5. The manufacture of ordinary nitre from Chilian sodium nitrate, begun in Germany on a larger scale for the supply of Russia during the Crimean War, has become an established industry, the saline residue from the vinasse of beet-root molasses distillation and the potassium chloride from Stassfurt carnallite

being in turn used as the source of the potassium — the latter much the more extensively at present. To no small extent has this process permitted the purchase of Indian saltpetre to be dispensed with, practically removing it from the market of several countries of Continental Europe.

*Potassium chloride.*—One of the greatest of new industries based upon saline products is certainly the manufacture of this compound from the great beds of carnallite, crude sylvine, &c., overlying the rock salt of Stassfurt and Kalucz. The process is essentially the simple repetition of crystallizations from solutions in which the double salts of magnesium and potassium are broken up, but in its details the method involves nice attention to the varying character of the crude saline mass treated, to the strength of the solutions at various stages, to the temperature, and to the time permitted for crystallization. In the regulation of temperature, steam-jackets to the pans and coils of steam pipe furnish most useful aid, as they do in a host of other processes of modern chemical industry. Much judgment has, moreover, been shown in determining the extent to which the process of purification may be profitably carried in order to supply the different demands of chemical manufactures and of agriculture.

*Potassium sulphate.*—This salt is also obtained from the material furnished by the Stassfurt beds, and on a much larger scale than was practicable before the discovery of these valuable sources of supply. It has been made by the action of sulphuric acid upon potassium chloride, in decomposing pans like those used in the first stage of the Leblanc soda process, and turning out a product analogous to the common "salt cake," but to a much larger extent from the potassium chloride of carnallite by double decomposition with the magnesium sulphate occurring in adjoining beds as kieserite, or obtainable by the action of water on kainite from other portions of the same remarkable series of deposits.

It is not yet twenty years since these potassium salts were but sparingly obtained by-products from the evaporation of sea-water and from kelp-working. They now represent of themselves important branches of industry, and have served to give new vigor to all manufactures in which potassium compounds are necessary materials.

*Potassium chlorate.*—The production of this salt has acquired increased importance from its fast extending use in calico-printing and in medicine, as well as in pyrotechny and the making of some kinds of friction matches. The older method of producing it, by passing chlorine into a hot solution of potassium carbonate, has become quite obsolete, and is replaced by the action of chlorine upon milk of lime, followed by conversion of calcium chlorate into the corresponding potassium salt by means of potassium chloride, thus avoiding the

measurable waste of potassium by conversion of a dearer into a cheaper salt (carbonate into chloride) to the extent of five-sixths of the whole amount used, and rendering the process at the same time more manageable and well defined. It is interesting to observe that the use of lime was first suggested (though not quite in the way afterwards proposed by Liebig and now practiced) by Graham, whose name we are much more accustomed to associate with researches in pure chemistry and physics than with technical improvements, though for the importance of the latter he seems ever to have had a lively interest.

*Potassium pyro-chromate.*—For this there is also increased demand owing to extended and varied use, chiefly in dyeing (logwood black, &c.), preparation of pigments for painters' use, and for pigment printing (with chrome yellow, vert Guignet, &c.), and as an oxidizing agent. New sources of supply of the raw material for its manufacture, chromite, have been opened in various directions, including localities in Australia, New Zealand and New Caledonia. The chromite of western North Carolina does not seem to be yet worked, probably on account of defective means of transportation. The use of lime in the roasting of the ore, replacing in part, or sometimes altogether, the potash or more expensive nitre formerly used, proves of much advantage by preventing clear fusion of the alkaline material with subsidence of the heavy ore out of reach of atmospheric oxygen, while potassium sulphate affords the means of converting the calcium salt formed into one of potassium.

*Potassium ferro-cyanide.*—The history of this salt for some years past has been one of declining production for more direct use in developing dyers' and calico-printers' colors, Prussian blue having been in large measure replaced by the coal-tar colors and ultramarine; but, on the other hand, of increased consumption in making potassium cyanide for the purposes of the electro-plater and photographer. The immense loss of nitrogen, at least 75 per cent. of that contained in the animal matter used, and no small loss of potash, leave this manufacture in the list of those still much needing improvement. The main conditions for diminishing the waste of organic nitrogen being a high temperature, thorough exclusion of air, and rapid heating up of the solid materials introduced into the furnace, it would seem worth trial whether advantage would not be derived from a mechanically regulated feed of very small charges rapidly following each other into a Siemens furnace with non-oxidizing atmosphere. This salt has within the last few years come to be a minor secondary product of the Leblanc process as applied to making potassium carbonate from the Stassfurt chloride. Recent patents for the manufacture of potassium ferro-cyanide from ammo-

mium sulpho-cyanate of gas liquor, or from the same salt made by the action of ammonia on carbon disulphide, seem to be still in the experimental stage only.

*Potassium cyanide*.—The manufacture of this now largely used compound presents nothing specially new since Liebig's process—fusion together of potassium ferro-cyanide and carbonate—came generally into use, save that soda is often added, and so a mixed product of potassium and sodium cyanides is obtained. No economically successful process has yet been secured for making this or other cyanides from atmospheric nitrogen, in spite of the numerous attempts at producing such a result.

*Sodium chloride*.—With ever-increasing consumption of common salt, there is little to note of recent important changes in the methods of preparation. In working the mother-liquors from the Mediterranean "salt gardens," the necessity for great storage reservoirs, in which to keep the concentrated solution over until it may be crystallized in the cold weather of winter, has been obviated by the introduction of machinery for the production of artificial cold; but the importance of working these mother-liquors has been much diminished by the products having now to compete with those from the Stassfurt deposits.

*Sodium nitrate*.—The very simple process of solution and crystallization by which the "Chili saltpetre" of South America is obtained admits of little modification, but the work has been systematized of late years and carried out with improved mechanical arrangements and upon a much larger scale than formerly, so as to provide for the greatly increased demand both for agricultural and manufacturing use.

*Sodium sulphate*.—The most interesting advance in the manufacture of this salt, so largely in demand for modern glass-making, has been its production by the mutual decomposition of common salt and kieserite (magnesium sulphate), both furnished by the Stassfurt beds. The purity of the product gives it the advantage over ordinary "salt-cake" for the glass manufacture.

*Borax*.—Greatly increased production is chiefly to be noted, due mainly to the discovery of new sources of supply of the raw material, partly the boro-natro-calcite ("tiza") of South America and the boracite of Stassfurt, but much more the great quantities of crude borax and "tiza" of California and Nevada. Extending use of the salt is observable chiefly in the manufacture of pottery and in connection with washing, but this is hardly in proportion to the greatly increased abundance and lower price.

*Ammonium chloride*.—The recent proposal of Gerlach deserves attention—namely, to work the "ammonia-soda" process with a view to producing sal-ammoniac, making the

sodium carbonate obtained a secondary product only, and not regenerating the ammonia. To this end gas liquor, or that from bone-black works, is to be simply distilled—best in some such apparatus as that of Solvay—the concentrated distillate mixed with brine and treated with carbon dioxide gas under pressure, the precipitated acid carbonate of sodium removed, some ammonium carbonate recovered from the residual solution by distillation, and ammonium chloride then crystallized out, separating it from remaining common salt. A similar process is proposed for making ammonium sulphate and nitrate. It may be worth noticing in relation to these salts, for which the demand is constantly increasing, that enormous waste of ammoniacal liquor prevails, or did but a few years back, at most of the gas works of the United States.

*Calcium chloride.*—Attention has already been drawn to the great importance of devising a workable process for economically making from this salt and from the corresponding magnesium compound hydrochloric acid or free chlorine. To the list of many other industries which tend to turn out more and more calcium chloride as a waste product may be added salt-boiling in certain regions, as in Ohio, where the mother-liquors are loaded with it.

*Calcium acid phosphate.*—The immense extension which the trade in “super-phosphate of lime” has taken of late years has led to many small improvements in the mechanical appliances of the manufacture, and some small changes in the chemical treatment used, so as to adapt it to the various phosphatic materials brought into the market, but no change of general importance has been made.

*Magnesium sulphate.*—The various methods formerly depended upon for the production of this salt have lost interest in view of the immense masses of kieserite found in the upper portion of the Stassfurt beds, this requiring only somewhat prolonged treatment with water to get it into solution, and subsequent crystallization. Although used for a larger number of purposes than heretofore, including sundry applications requiring a cheap soluble sulphate, the price is very low and the available supply in excess of the demand.

*Aluminum sulphate.*—This salt, though always open to the objection of variability of constitution as it reaches the market, has been made of better quality of late than in former years, more nearly definite in character and freer from iron. Especially is this true of the so-called “porous alum” made from kryolite. Under the name “alum clay cake,” that made from clay and still retaining silica in admixture with it finds extensive use among paper-makers and for some of the less refined processes of dyeing, and is manufactured upon an increasing scale, both for such direct use and for conversion into alum.

*Alum.*—The working of alum shale and alum earth, though still practiced upon a very large scale, has of late years been relatively falling behind, some large establishments having even been abandoned, while clay, beauxite and cryolite have assumed increased importance as sources of the aluminum required, sodium aluminate being first made from the two latter, partly used as such and partly converted into alum. In working shale, moreover, sulphuric acid is largely used now, instead of depending upon the oxidation of the disseminated pyrites.

As regards the alkaline sulphate used in making the double salt, the tendency for a number of years has been towards the substitution of potassium by ammonium sulphate, but this has to some extent been checked, particularly in Germany, by the abundant supplies of potassium compounds from Stassfurt.

*Iron (ferrous) and copper sulphates.*—Nothing of special importance as to these heavy-metal salts requires notice, except that an extension has been given to the material for their manufacture as secondary products of metallurgic operations, in the growing production of "cementation" copper in the wet way, and in the extraction of gold and silver from copper regulus or copper mattes employed as the means of concentrating the precious metals.

J. W. MALLET.

(To be continued.)

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#### REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

(Continued from p. 291.)

*Potassium.*—R. Hornberger\* has shown that the method usually employed for the determination of the alkalies in the ashes of plants is defective, inasmuch as the solution containing these as chlorides—and from which all other constituents of the ashes are supposed to have been removed—still contains phosphoric acid. Hence an error is made in considering as chloride of sodium the difference between the weight of the residue remaining after the evaporation and the amount of chloride of potassium found by means of platinum chloride. The presence of phosphoric acid in this solution is due to the decomposition of phosphate of calcium by carbonate of ammonium, when this reagent, ammonia and oxalate of ammonium are added to the ash solution for the purpose of removing other constituents than the alkalies. It is therefore proposed to precipitate the phosphoric acid as phosphate of calcium by means of ammonia, and remove it by filtration before adding the carbonate and oxalate of ammonium.

\* Zeitsch. anal. Ch. 18, 361.

H. Precht\* announces that the method proposed by A. Carnot† for the volumetric estimation of potassium by means of subnitrate of bismuth, hyposulphite of sodium and a standard solution of iodine does not yield satisfactory results.

*Lithium*.—C. Rammelsberg‡ has confirmed, by means of new experiments, his former assertion that the precipitate obtained by treating a solution of a lithium salt with phosphate of sodium is in all cases a sodium lithium phosphate; and hence that lithium cannot be correctly determined by the method of Mayer.

*Magnesium*.—Schlagdenhauffen§ proposes as a sensitive reagent for magnesium a solution obtained by dissolving iodine in two per cent. caustic potassa or soda until its color becomes golden-yellow. This reagent produces a brownish-red precipitate, or reddish coloration in very dilute solutions of magnesium sulphate or chloride; and the presence of barium, strontium or calcium does not interfere with the detection of magnesium by means of it.

*Zinc*.—C. Mann|| determines zinc indirectly by treating the washed sulphide—obtained by conducting sulphide of hydrogen into the acetic acid solution—with moist chloride of silver, and ascertaining by means of Volhard's method the amount of chlorine which passes into solution as chloride of zinc. According to the author the exchange of sulphur for chlorine between zinc and silver takes place rapidly at the boiling temperature of water.

To determine zinc electrolytically, F. Beilstein and L. Jawein¶ treat the solution of sulphate or nitrate with caustic soda until a precipitate forms, then with cyanide of potassium until a clear solution is obtained, insert the platinum electrode, and connect with a Bunsen's battery consisting of four cells. The zinc precipitates at the rate of about 0.1 gr. per hour.

*Cadmium*.—To determine cadmium electrolytically, Beilstein and Jawein\*\* dissolve the sulphide or oxide in nitric acid, neutralize with caustic potassa, add cyanide of potassium until the precipitate is barely dissolved, dilute so that 75 c. c. of the solution contain only about 0.2 gr. of cadmium, place the beaker in a vessel of cold water, insert the electrode, and connect with a Bunsen's battery of three cells. The average precipitation of cadmium is 0.080–0.090 gr. per hour.

*Silver*.—Bronner†† describes how the gas furnace invented by Dr. Hempel‡‡ may be advantageously employed for the purpose of illustrating the process of cupellation, and even for quantitative assaying.

\* Ber. d. chem. Gesell. 12, 1134—from Correspondenzb. des Ver. analyt. Chemiker. 6–10.

† Comptes rendus, 83, 390; 84, 1504; 85, 301; 86, 478.

‡ Jour. Chem. Soc. 1879, 18.

§ Zeitsch. anal. Ch. 18, 162.

\*\* Ber. d. chem. Gesell. 12, 759.

†† Zeitsch. anal. Ch. 16, 454.

‡ Zeitsch. anal. Ch. 18, 97.

¶ Ber. d. chem. Gesell. 12, 446.

|| Zeitsch. anal. Ch. 18, 81.

*Mercury*.—J. W. Bruehl\* recommends agitation with a dilute solution of chromic acid as the most effectual method of purifying mercury.† L. Meyer‡ describes a modification of the apparatus formerly proposed by him§ for the purification of mercury, in which he makes use of ferric chloride instead of nitric acid.|| G. Attwood¶—“Quantitative Assay of the Ores and Compounds of Mercury by the Blowpipe.”

*Cobalt*.—G. Papasogli\*\* and T. Tattersall†† announce that minute quantities of cobalt may be detected by means of the red color developed by yellow sulphide of ammonium in a solution of cobaltocyanide of potassium. The presence of cyanide of nickel or any other soluble cyanides, except that of copper, does not interfere with the reaction. Papasogli and also H. W. Wiley‡‡ found it possible by means of this test to detect with certainty the presence of 0.0001 gr. of a cobaltous salt when dissolved in 1 c. c. of water.

*Iron*.—C. Doelter§§ describes an arrangement of apparatus which may be used with advantage in decomposing silicates with sulphuric and hydrofluoric acids, when it is desired to determine the ferrous iron contained in them by means of permanganate of potassium.

W. F. K. Stock:|||| “On a new Form of Apparatus for the Production of Ferrous Salts for Titration.”

*Manganese*.—F. Kessler:¶¶ “On the Determination of Manganese, especially in Iron-Manganese Alloys.”

To determine manganese, C. Roessler\*\*\* makes use of the fact that, when a solution containing a manganous salt and nitrate of silver is treated with an alkali, a precipitate is obtained which contains fixed relative quantities of the two metals, namely  $\text{Ag}_4\text{O} \cdot \text{Mn}_2\text{O}_3$ . The solution of manganous salt, which must be free from substances that precipitate silver or reduce the nitrate, is placed in a measuring flask; a measured quantity of a standard solution of silver nitrate, more than is required for the precipitation of the manganese, added; the flask heated upon the water bath, and both manganese and the excess of silver precipitated by means of carbonate of sodium. Ammonia is now added, the flask cooled and filled to the mark, a part of the contents filtered off through a dry paper, and the excess of silver in a measured portion of the filtrate determined by means of Volhard's method. The presence of ferric iron does not interfere with the determination of manganese by this method. The author has found it necessary, however, in the case of solutions of iron-manganese alloys to first remove the iron by means of acetate of sodium,

\* Ber. d. chem. Gesell. 12, 204.

† Ber. d. chem. Gesell. 12, 437.

‡ This Journal, 1, 213.

§ Ber. d. chem. Gesell. 12, 297—orig. Gazz. Chim. ital.

|| Chem. News, 39, 66.

§§ Zeitsch. anal. Ch. 18, 50.

¶¶ Zeitsch. anal. Ch. 18, 1.

† This Journal, 1, 68.

§ Zeitsch. anal. Ch. 2, 241.

¶ Jour. Chem. Soc. 1879, 207.

¶¶ This Journal, 1, 211.

|| Chem. News, 39, 46.

\*\*\* Ber. d. chem. Gesell. 12, 925.

since such solutions, previous to the removal of the iron, contain substances which reduce the nitrate of silver.

J. Pattinson\* has ascertained that all the manganese in a manganous salt may be precipitated in a state of oxidation equivalent to that of the metal in the superoxide, if the solution containing it and an equal or larger amount of ferric chloride is treated with hypochlorite of calcium or bromine, the temperature raised to 60° or 70°, and an excess of calcium carbonate added. The author utilizes this fact in the determination of manganese in manganiferous iron ores, &c., by an indirect volumetric method.

*Chromium*.—E. Donath† detects chromate of potassium in the presence of bichromate by means of manganese sulphate, bichromate in the presence of chromate by treating with a hot solution of sodium hyposulphite, and free chromic acid in the presence of bichromate by means of potassium iodide.

W. J. Sell‡ converts chromous compounds into chromic acid by slowly adding to their acidified, boiling solutions a dilute solution of permanganate of potassium until the color of the latter no longer disappears. The conversion is complete; but, since the reduction of the permanganate towards the end of the reaction is only partial, the method cannot be employed to determine chromium volumetrically. To do this the author, after having rendered the solution alkaline with carbonate of sodium, added alcohol and filtered, makes use of the iodine method. To decompose chrome iron ore he recommends fusion, first with potassium hydrofluoride or sodium fluoride and acid sodium sulphate, and then with acid sodium sulphate alone.

*Gold*.—H. von Jueptner:§ “On the Separation of Gold and Silver, and on the Determination of the same in Alloys.”

*Lead*.—To determine minute quantities of lead in solution colorimetrically, G. Bischoff|| evaporates to dryness, ignites the residue, digests with the least possible excess of pure hydrochloric acid, filters, washes, conducts sulphide of hydrogen into the filtrate, neutralizes with ammonia, and finally acidifies with hydrochloric acid.

*Vanadium*.—O. Lindemann¶ determines vanadic acid volumetrically by titrating in an acid solution with ferrous ammonium sulphate, which has been strongly acidified with sulphuric acid. The vanadic acid or the corresponding anhydride is reduced to the dioxide. Ferricyanide of potassium, with which a small portion of the solution is from time to time tested, serves to indicate the completion of the reduction. The presence of salts of iron, aluminium, chromium, and the alkalies does not diminish the accuracy of the results.

*Hydrocarbons*.—W. Hempel\*\* finds, that if a mixture of free

\* Jour. Chem. Soc. 1879, 365.

† Jour. Chem. Soc. 1879, 292.

‡ Zeitsch. anal. Ch. 18, 73.

§ Zeitsch. anal. Ch. 18, 78.

|| Zeitsch. anal. Ch. 18, 104.

¶ Zeitsch. anal. Ch. 18, 99.

\*\* Ber. d. chem. Gesell. 12, 1006.

hydrogen, marsh gas and atmospheric air is passed over superficially oxidized palladium under such conditions that the temperature cannot rise above  $100^{\circ}$ , the hydrogen is completely converted into water, while the marsh gas is wholly unaffected. Mallard and Le Chatelier\* recommend the use of the hydrogen flame as a means for detecting the presence of fire-damp in mines. The flame becomes distinctly blue when the atmosphere contains 0.25 per cent. of marsh gas; while at least 3 per cent. is necessary to produce the same effect upon the flame of the ordinary miner's lamp, even when a blue glass is used.

R. Angus Smith:† “Detection of Fire-Damp.”

*Hydroxyl Derivatives of Hydrocarbons.*—Ch. Bardy and L. Bordet‡ describe in detail their procedure in determining the methyl alcohol contained in commercial methylenes by Krell's method.§

H. R. Proctor||: “Weselsky's Reaction for Phloroglucin.”

*Organic Acids, Esters and Salts.*—To determine acetic acid contained in wine, L. Weigert¶ places a flask containing a measured amount of it in a water bath filled with a strong solution of common salt, and distils under diminished pressure. Water is added to the residue, and the distillation repeated as often as may be necessary, and the quantity of the acid ascertained by means of a standard solution of alkali. A. Stromeyer\*\* states that to ascertain the value of crude commercial acetate of calcium, the acetic acid should be determined, instead of relying on a determination of the calcium as is frequently done; since, by the latter practice, results too high by 4-5 per cent. are obtained.

In order to obtain further confirmation of the presence of so-called ethyldiacetic acid in a urine, which gave the characteristic dark cherry-red color when treated with ferric chloride, A. Hilger†† mixed 300 c. c. of the urine with 50-60 c. c. of concentrated hydrochloric acid, and distilled off two-thirds of the volume. The residue gave no reaction with ferric chloride. The distillate, however, smelled strongly of acetone, and yielded crystals of iodoform when treated with potassium hydroxide and a solution of iodine in potassium iodide. To further prove the presence of both acetone and ethyl alcohol in the distillate, it was subjected to fractional distillation, and the fractions treated with chromic acid. The portion collected at and under  $56^{\circ}$  yielded on oxidation formic acid; while that collected after the temperature had risen above  $56^{\circ}$ , was free from the odor of acetone, yielded the iodoform reaction, and on oxidation, acetic acid and carbon

\* Comptes rendus. 88, 749.

† Chem. News, 39, 267.

‡ Bull. de la Soc. Chim. 32, 4.

§ Ber. d. chem. Gesell. 6, 1030; 7, 1192; 9, 1928.

¶ Chem. News, 39, 245.

|| Zeitsch. anal. Ch. 18, 207.

\*\* Ber. d. chem. Gesell. 12, 1135; orig. in Correspondenzb. d. Vereins analyt. Chemiker.

†† Liebig's Annalen, 195, 314.

dioxide. To determine approximately the amount of ethyl-diacetic acid contained in the urine, 60, 80, or 100 c. c. were mixed with strong hydrochloric acid, and distilled as before; the distillate treated with potassium hydroxide and a strong solution of iodine in iodide of potassium, gently warmed, and allowed to stand in a closed vessel twenty-four hours. The iodoform was then collected in a weighed filter paper, washed with cold water, dried over sulphuric acid and weighed. In this manner, closely agreeing results were obtained from different portions of the same urine.

B. E. Dietzell and M. G. Kressner:\* "Investigation of Butter Fat."

J. Koettstorfer† proposes, as a new method for detecting the presence of foreign fats in butter, to determine the quantity of caustic potassa required for the complete saponification of a given weight of it. The author found as the result of an examination of thirteen specimens that one gram of unadulterated butter requires for its saponification between 0.2215 and 0.2324 gr. of potassium hydroxide, while the same weight of other fats required in no case more than 0.197 gr.

E. Reichert‡ has published a method for the analysis of butter which is based on the fact that the proportion of volatile acids in butter is much larger than in other fats. He saponifies a given weight of the material under examination, decomposes the product with sulphuric acid, distils and titrates the acids in the distillate with a standard solution of caustic soda.

According to A. Guyard,§ a saturated boiling solution of oxalic acid decomposes chlorates, bromates and iodates with liberation of a portion of the chlorine, bromine and iodine, and the reaction may be employed with advantage to detect the presence of these salts. If a solution containing the three is treated with a sufficient quantity of oxalic acid, the chlorate is completely decomposed and the free chlorine driven out by the aqueous vapor and carbon dioxide, while the bromate and iodate remain intact. The addition of more acid, however, immediately induces a decomposition of the bromate. This second stage of the reaction, too, is completed and the free bromine expelled before the third, the decomposition of the iodate, begins.

H. Schiff and S. Pagliani|| find that the characteristic reaction of salicylic acid with ferric chloride is prevented when 400 parts of sulphuric, 385 of nitric, or 36 of hydrochloric acid are present.

In order to detect salicylic acid in beer and similar dark-colored liquids by means of ferric chloride, Aubry¶ subjects them to dialysis. Blas,\*\* having examined the different

\* Zeitsch. anal. Ch. 18, 83.

† Ibid. 18, 199.

‡ Ibid. 18, 68.

§ Bull. de la Soc. Chim. 31, 299.

| Ber. d. chem. Gesell. 12, 385.

¶ Ber. der chem. Gesell. 12, 1135—orig. in Correspondenzb. d. Vereins analyt. Chemiker.

\*\* Jour. f. prak. Chemie, 19, 43.

methods recommended for the detection of salicylic acid in beer, concludes that it is simplest and surest to test the urine with ferric chloride a few hours after the consumption of the beer. In this manner the acid may be readily detected when the beer contains only 0.025 gr. to the liter.

*Carbohydrates.*—F. W. Pavy\* has published a method for the volumetric determination of glucose which is founded on the fact that a solution of the sugar reduces and decolorizes an ammoniated Fehling's solution without precipitation. The end of the reaction is indicated by the disappearance of the last traces of color from the copper solution. Pavy states that when 100 c. c. of Fehling's solution is mixed with 300 c. c. of ammonia of 0.880 sp. gr. and 600 c. c. of water, one molecule of sugar reduces six atoms of copper from the cupric to the cuprous condition, instead of five, as in the ordinary Fehling's solution. The addition of one gram of potash to 20 c. c. of the solution thus obtained does not alter the ratio of sugar decomposed to copper reduced. If, however, more than one gram and less than five is added, the relation is 1 : 5—6; while when five or more grams are added it is 1 : 5, as in the ordinary Fehling's solution. He therefore recommends the use of a solution which is obtained by mixing 120 c. c. of Fehling's solution with 300 c. c. of ammonia of 0.88 sp. gr. and diluting to 1000 c. c. 100 c. c. of this will produce the same reducing effect as 10 c. c. of Fehling's solution.

O. Hehner† has examined the method and found it capable of yielding excellent results when the original Fehling's solution contains between 120 and 150 gr. of sodium hydroxide per liter. Between these limits the relation of sugar to copper given by Pavy (1 : 6) holds good, but not otherwise. A controversy has arisen between P. Cazaneuve, D'Arsonval and P. Picard with respect to the merits of Cl. Bernard's method for the determination of glucose in blood.‡

E. Salkowski§ “On the Compounds of Grape-Sugar with cupric Hydroxide.”

J. Riban|| “On the Transformation of Starch into Glucose by Cold Water.”

To determine quantitatively the amount of starch in sausage, L. Medicus and E. Schwab¶ decompose it by means of a diastase solution, treat the products with a little hydrochloric or sulphuric acid, and estimate the grape sugar thus produced by titrating with Fehling's solution.

*Nitro Compounds.*—F. Hess\*\* : “On the Separation of Nitro-glycerin from Nitrocellulose.”

*Alkaloids.*—Dragendorff†† : “On a New Brucine Reaction.”

E. Dannenberg‡‡ : “Detection of Colchicine in Cases of Poisoning.”

H. N. MORSE.

\* Chem. News, 39, 77. †Ibid. 39, 197. ‡Comptes rendus, 88: 595, 753, 755 and 864.

§ Zeitsch. anal. Ch. 3, 79.

|| Bull. de la Soc. Chim. 31, 10.

¶ Ber. d. chem. Gesell. 12, 1285.

\*\* Zeitsch. anal. Ch. 18, 352.

†† Zeitsch. anal. Ch. 18, 107.

‡‡ Zeitsch. anal. Ch. 18, 129.

## NOTES.

*A Device for the rapid Filtration of the Carbon in Cast Iron and Steel Analyses.*

In the analysis of cast iron and steel, much time is consumed in the separation of the carbon by filtration. Even under the most favorable circumstances the operation requires several hours. All attempts at rapid filtration by Bunsen's method, using the usual asbestos filter, proved unsuccessful. The increased pressure either forced the plug of asbestos through the funnel, or if the asbestos was more closely packed, the filtration was rendered exceedingly slow. In order to overcome this defect if possible, a piece of apparatus was constructed, which seems to fulfil all the requirements very successfully.

A piece of platinum foil about .01 mm. in thickness, is cut into a disc, having very near the same diameter as the funnel used, which latter is of the same kind ordinarily used in the estimation of carbon. This disc (Fig. 1.) is perforated with five or six holes, about 1 mm. in diameter, and to its centre at right angles to its plane is soldered, with a minute piece of gold, a stout platinum wire about 1 mm. in diameter, and of such a length that it may extend a short distance below the contracted portion of the funnel (Fig. 2). When the disc is in position, the wire extends down through the smaller portion of the funnel, and tends to keep the platinum plate always horizontal (Fig. 3). Upon this plate is placed a thin layer of pure asbestos. The lower portion of the funnel may be placed through the cork of the receiver of a Bunsen's pump or any other convenient aspirator, as in the usual method of rapid filtration.



Fig. 1.



Fig. 2.

The asbestos should be moistened, and the pump set in action before the filtration commences, in order that the asbestos may become well packed before the finely divided precipitate is thrown upon it.

After the operation is finished, and the precipitate well washed, the pump should be allowed to run for a few minutes in order that the precipitate may

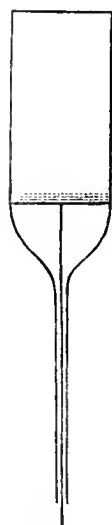


Fig. 3.

become comparatively dry. In the state in which the carbon now remains, it may be pushed out of the funnel in a solid coherent cake, by pressure applied to the projecting platinum wire. The tube only requires to be wiped with a small piece of asbestos to render it perfectly clean from the adhering precipitate.

With this apparatus, a filtration which, under ordinary circumstances, would occupy several hours, requires but from twenty minutes to half an hour for its completion.

J. CREAGH SMITH.

UNIVERSITY OF PENNSYLVANIA, Nov. 1879.

### *Potassium Permanganate and the Strychnine Test.*

However unsatisfactory they may be, the color reactions of strychnine are still in common use. After dissolving the suspected substance in strong sulphuric acid, it has been customary to add small bits of some oxydizing agent, such as the dichromate or permanganate of potassium, or the dioxides of lead or manganese, and to note the colors which follow.

The permanganate was introduced by W. A. Guy,\* who claimed for it superiority to the dichromate, and peculiar excellence in respect to brilliancy and delicacy of reaction. As is well known, however, the strong acid present may act upon the salt; slowly, when cold, more quickly when warm, causing evolution of oxygen and vapors of permanganic acid;† at the same time more heat is developed, the vapors rise and condense above the liquid in a lustrous film, in which rose-colored drops shortly appear, and finally undergo still further changes of color. Of course the mixture absorbs water with great avidity, and it is asserted by Terreil‡ that the solution of permanganic acid with sulphuric acid containing three atoms of water is violet in color. Wurtz§ describes the solution of permanganic acid as of a beautiful red crimson by reflected light, violet by transparent light, and of very great coloring power. It is also known that the solutions of manganic and permanganic salts are colored by many reducing agents,|| and it is a fact easily shown, that if readily decomposable organic matter is present, as is often the case in toxical work, the reaction may occur with destructive energy. It will be seen that these reactions, while not necessarily leading to errors, may, nevertheless, under varying conditions, give colors uncomfortably like some of those to be looked for.

Wenzell,¶ by a long series of experiments, arrived at the

\* Pharm. Journal and Trans. 1861, pp. 558, 602, &c.

† Watts, Dict. Chem. 3, p. 819; also, Second Supp., p. 772.

‡ Quoted by Watts, Dict. Chem. 3, 820.

§ Dict. Chimie, p. 300.

|| Rammelsberg, Leitfaden, &c., 1874, p. 34.

¶ Am. Jour. Pharm. 1870, p. 355.

opinion that the permanganate gives the most delicate reaction, thus confirming the statement of Guy. His results have been widely quoted, though they have not displaced the use of the dichromate; many still adhering to the latter as altogether superior; others, as Fresenius,\* according to the permanganate equal rank.

I had tested for strychnine the extract from an infusion of *eupatorium*, mentioned in the succeeding note, using dichromate and dioxide of manganese, and had obtained no blue coloration whatever. Using permanganate, however, I secured a most magnificent bluish purple, which was usually developed somewhat slowly, and remained for some time, but at length faded into a dirty reddish brown. Blank experiments showed no such coloration, but if, into one of these a piece of filter paper were let fall, the same blue color soon appeared. Further experiments show that not only filter paper, but bits of woody fibre, tea paper and shreds of cloth give the same reaction, and in one case, very nearly the proper succession of strychnine colors was obtained. The reaction is so delicate that if two dishes are properly cleaned, rinsed with distilled water and dried, one by heat, the other by a clean towel or a sheet of filter paper, the former will give no reaction, the latter a very perceptible blue. Reese† states that the production of a violet color has been noticed in the case of various organic matters by at least one other observer, but does not reject the permanganate on that account. It is not claimed that the succession of colors given by strychnine is ordinarily developed; yet, in view of the possible colors which may arise from the reagents alone, giving nearly every required shade except blue; and in view of the fact that many substances, if present, will afford early in the reaction a very striking blue color; we ought, hereafter, to limit the use of permanganate rigorously to work upon the pure alkaloid. Its employment in toxical cases, where even a minute amount of organic matter may be present, so long as dichromate may be had, is not only unnecessary but dangerous.

W. T. SEDGWICK.

### *The Relations of Eupatorium and Strychnine.*

In a case of suspected poisoning by strychnine which was before the courts not long ago, the affidavit of the chemist employed by the State to make an examination for strychnine reads, according to the newspaper report, as follows: “. . . . The residue obtained from the alcohol in which the stomach was preserved gave, faintly, one of the reactions of strychnine . . . . when dissolved in sulphuric acid and treated with

\* Qualitative Analysis.

† Manual of Toxicology, 1874.

bichromate of potash. As the alkaloid 'curare' produces a similar play of colors, and it is stated that they have been had from organic matter alone, *and I have found them to appear in the extract from an infusion of boneset similarly treated*, it is necessary to insist upon all the other characteristic proofs to identify strychnine. . . ." It should be added that the italics are mine, and that special importance attached to this remark because the deceased had drunk largely of boneset (*eupatorium*) just before his death. Not having met the statement elsewhere, and knowing the very extensive use of the plant as a domestic remedy with no recorded case of lethal effects produced by it, I determined to experiment for myself. Accordingly, in August when the plants were just coming into blossom, I collected a very large supply, dried it in a hot room, pulverized by means of a hay cutter and a drug mill a large amount, using for the purpose the whole plant except the root. Twelve litres of water were brought to 100° in a copper dish and seven hundred grams of the pulverized product put in, the whole kept just below 100° for several hours, and finally filtered hot through cloth and paper. The filtrate was now concentrated over the water-bath and filtered from time to time, the precipitates being preserved. The mass which had been extracted with water was now treated with sulphuric acid, so that the latter was of .2 per cent. strength, and kept warm for some time, the liquid filtered off and also concentrated. An attempt was made to dialyse some of the fluid, in the hope of getting rid of coloring matter and of securing, outside, a sulphate of the alkaloid if any existed. It met with no success.

The aqueous extract having become very concentrated, so that it was black, heavy and bitter, an attempt was made to separate from it any strychnine or other alkaloid which might have been present. Some of the liquid was made alkaline with dilute ammonia, ether was added, the whole well shaken and allowed to stand in a separating funnel. Meanwhile some of the same concentrated solution had been carried to dryness over the water-bath, yielding a black, hard and shining extract of very bitter taste. Tests were then made with sulphuric acid and successively dichromate of potassium, dioxide of manganese and permanganate of potassium. Neither the extract from the ether, which was yellowish, amorphous and exceedingly bitter, though scanty, nor the aqueous extract, nor any of the various precipitates obtained by concentration, nor the result of extraction made afterward with ether in acid solution and with chloroform, gave the slightest indication of any reaction similar to that given by strychnine when the dichromate or peroxide was used. The permanganate, however, yielded a beautiful blue passing in some cases into reddish colors, so that but for the discovery described in the

preceding paper I should have suspected a reaction similar to strychnine as belonging to *Eupatorium perfoliatum*, L. The extract with sulphuric acid gave results precisely similar, so that I utterly failed to get reactions which would lead to confusion of *eupatorium* with strychnine.

Since making my experiments I learn that Dr. Antisell of the U. S. Patent Office has been led by the obvious importance of the subject to make a similar investigation, and has also completely failed to get any strychnine reaction from either the aqueous or alcoholic extract by using sulphuric acid and dichromate of potassium, with which alone he worked. I have been told that physiological effects have been attributed to *eupatorium* similar to those produced by strychnine. Some experiments which I have lately made upon frogs do not show the least resemblance between them.

W. T. SEDGWICK.

JOHNS HOPKINS UNIVERSITY, Nov. 1879.

### *Latest Developments in the Chlorine Question.*

F. SEELHEIM has described an experiment which he has performed, showing that the metal platinum is slowly converted into vapor when heated in a current of chlorine gas. He considers this fact in its bearings upon Victor Meyer's recent experiments on the specific gravity of chlorine at high temperatures, and concludes that Meyer's results are entirely vitiated by it. It will be remembered that Meyer, in his experiments, used platinous chloride,  $\text{Pt}_2\text{Cl}_6$ , and assumed that all the chlorine of this compound is liberated at the temperature employed, while the platinum remains behind.—(*Ber. d. chem. Gesell.* 12, 2066.)

V. MEYER has replied to Seelheim, saying that in his experiments the platinum from the platinous chloride is always found in the form of a solid mass, weighing almost exactly what it should weigh if none of it were converted into vapor. He has further found that the amount of platinum actually converted into vapor when heated in a rapid current of chlorine, is exceedingly small—so small that it could not possibly exert an appreciable influence on the results. More than this, iodine, which is used in the solid form, gives results analogous to those reached in connection with chlorine.—(*Ber. d. chem. Gesell.* 12, 2202.)

### *Conservatism in Chemistry.*

SAINTE-CLAIRE DEVILLE, in commenting on the recent discussions concerning vapor densities in the French Academy, concluded his remarks in the following words: "For more than twenty years past I have endeavored in my teachings

and in my writings to combat the intervention of the idea of force in the sciences — of affinity and atomicity in chemistry, for example. I have sought, at least in teaching, to avoid hypotheses which are absolutely gratuitous, like the hypothesis of atoms, of molecules and of hypothetical states of matter, abstractions which always end by being incorporated. I am convinced that all which cannot be demonstrated ought to be rejected, that all which is useless in science is injurious, and I am of the opinion, with my learned friend M. Berthelot, that chemists are following a dangerous road which has been resolutely avoided for several years by the great minds who have laid the foundation of Thermodynamics, Thermochemistry and modern Physiology.

“Before speaking vaguely of gases and vapors, of their atoms, of their molecules, of their combination and their decomposition, it is necessary to study the analogies of gases with liquids, and even with solids, and to endeavor, not to find their constitution, as is said nowadays somewhat boldly, but to find their functions and what they have in common with the functions of substances which are more completely within the perception of our senses. This shall be the subject of a subsequent communication.”\*

#### *Action of Ozone on Carbon Monoxide.*

A. R. LEEDS\* has shown that, when carbon monoxide and oxygen are passed together through an improved ozonizing battery constructed by him, carbon dioxide is formed; while, if free ozone be brought together with carbon monoxide outside of the ozonizing battery, no union takes place. The latter result confirms that reached some years since by Remsen and Southworth. As Leeds worked with more concentrated ozone than has hitherto been used in like experiments, it seems now to be pretty firmly established that ozone cannot transform carbon monoxide into the dioxide, at least at ordinary temperatures. The transformation which takes place in the ozonizing battery is probably due to the unstable condition into which the oxygen is thrown by the conditions there surrounding it. It may be regarded as in the nascent state. This nascent oxygen probably effects two changes: 1st, that of a part of the oxygen into ozone, and, 2d, that of a part of the carbon monoxide into carbon dioxide.

\* We quote this remarkable passage, not because we are in thorough sympathy with the spirit of the speaker, but to call attention to the fact that Virchowism has its representatives in chemistry as well as in biology. If everything “which cannot be demonstrated ought to be rejected,” the impulse to original investigation would surely be much weaker than it now is. “Working hypotheses” are the salvation of any science — ED.

† Journal Am. Chem. Soc. 1, 450.

*The Future of Animal Tar.*

Not many years ago the substance known as coal-tar was regarded by chemists as well as by laymen in the light of an uninviting and almost hopelessly complex mixture. To-day, as is well known, it is the source of a large group of highly interesting bodies, and forms the basis of many important industries, some of which are still in their infancy. Certain recent developments in connection with animal tar seem to indicate that there is a future in store for this substance as interesting and as important as the present of coal-tar. It is obtained in largest quantity as a secondary product in factories in which bone-black is made by dry distillation of bones and other animal material. By fractional distillation the tar can be divided into several distinct portions, among which are the bases known as pyridine,  $C_5H_5N$ , and picoline,  $C_6H_7N$ , which are the first two members of an homologous series. Now, through the researches of Dewar,\* Ramsay,† Weidel,‡ Hofmann,§ and others, it has been shown that these bases are intimately connected with such alkaloids as quinine, cinchonine, cinchonidine, berberine, piperine and nicotine. All of these alkaloids when oxidized yield acids which are simple derivatives of pyridine or some other member of the series. The chemistry of the alkaloids is then, in all probability, to be discovered through a careful study of the bases of the pyridine series, and this probability has of late led a number of workers to turn their attention to these bases. It can fairly be prophesied that at no distant time our knowledge of the alkaloids will be materially increased through the aid of investigations now in progress.

\* Zeitschr. f. Chem. 1871, 116.

† Phil. mag. 1877, 246; Ber. d. chem. Gesell. 11, 325.

‡ Ann. d. Chem. 165, 328; 173, 176; Ber. d. chem. Gesell. 12, 1989.

§ Ber. d. chem. Gesell. 12, 984.

*RECENT PUBLICATIONS RELATING TO  
CHEMISTRY.*

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WURTZ, A. Elements of Modern Chemistry. Translated and edited by W. H. Greene, M. D. Philadelphia: Lippincott.

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# AMERICAN CHEMICAL JOURNAL.

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## A METHOD FOR THE PROXIMATE ANALYSIS OF PLANTS.

BY HENRY B. PARSONS.

At the request of my friend and former instructor, Prof. Albert B. Prescott, of the University of Michigan, I have prepared the following scheme for the analysis of plants. This method will appear, in substance, in his new Proximate Organic Analysis, now nearly completed.

The plan submitted is the outgrowth of a quite varied experience in the proximate analysis of plants; no claim to originality is made, the sole aim being to arrange in one simple scheme those methods best suited to insure accuracy.

It must be premised that no one method is applicable in all cases, and that the operator will so modify and adapt the proposed processes as to best attain the truths he seeks. If the present scheme shall serve merely as an example, to be improved upon as discoveries multiply, it will at least have served to stimulate to the more thorough study, this side the Atlantic, of a much neglected, yet very important, branch of analysis. The American student, when first entering upon the study of plant analysis, is perplexed and disheartened, owing to the lack of any elementary treatise in which he

may find directions for the quantitative estimation of the various plant constituents. The works of Rochleder and Wittstein, while giving most valuable assistance in the investigation of special constituents and their separation from large quantities of the crude herb, still fail to give clear and practicable directions for the quantitative estimation of each constituent. Von Mueller's latest enlarged edition of Wittstein's Plant Analysis gives a scheme, most excellent in many respects, yet cumbered with tiresome methods of extraction and manipulation, which serve to unnecessarily lengthen the time required for making the analyses without increasing the accuracy of results obtained.

Too many American analyses of plants have been summarized thus: "The plant contains gum, resin, tannin, a volatile oil, and a peculiar bitter principle, to which may be ascribed its medicinal activity." The foreign journals bring occasionally most excellent examples of accurate examinations of vegetable substances; as instances may be cited the examination of ginger, by J. C. Thresh,\* and of ergot,† alocs,‡ and other articles, by Prof. Dragendorff. To these sources the student must look for his best models, until a more thorough and systematic training is given American students in proximate organic analysis.

In following the plan now presented, the use of the apparatus for repercolation is strongly urged for the extractions with benzole, alcohol, and other volatile solvents. A very simple and inexpensive apparatus has been described by various American and foreign chemists.§

"In any convenient water-tight vessel is a worm of block tin pipe, having an internal diameter of 9 m. m., and a length of about 2.5 metres. The lower (external) part of this worm is fitted, by an ether-soaked, velvet cork, to a glass percolator having a diameter of 4 c. m., a length of 20 c. m. to the constriction, and 5 c. m. below. Within this percolator is a smaller tube, flanged at the top and bottom, and suspended by fine platinum or copper wires. This tube has a diameter of

\* *Phar. Jour. Trans.* [3], 10, 81. Aug. 1879.

† *Phar. Jour. Trans.* [3], 6, 1001. June 17, 1876.

‡ *Werthbestimmung*, 1874, p. 110.

§ B. Tollens, *Zeitsch. f. Anal. Chem.* [17], 320, 1878; *New Remedies*, [7], 335, Nov. 1878; W. O. Attwater, *Proc. Am. Chem. Soc.* [2], 2, p. 85; S. W. Johnson, *Am. Jour. Sci. Arts*, [12], 196; H. B. Parsons, *New Remedies*, [8], 293, Oct. 1879.

2.5 to 2.8 c. m., and a length of 14 c. m.; the bottom is covered by filter paper and fine washed linen,\* tied on by linen thread. The weighed sample of the finely powdered herb is placed within this tube for extraction. A light glass flask, weighing about thirty grams, is fitted by an ether-soaked cork to the outer percolator." Having introduced the solvent into this glass flask, the connections are made secure, and heat is applied, by a water-bath, to the flask. If the liquid is too slowly volatilized, the addition of a little common salt to the water in the bath serves to remove the trouble.

Next in importance is the use of a good tared filter. The form originally presented by F. A. Gooch† leaves little to be desired. It may be made by perforating with fine holes the bottom of an ordinary platinum crucible, and fitting it accurately to a perforation made in a large rubber cork; this cork connects it with a receiving vessel, which, in turn, is connected with a Bunsen's pump. Fine asbestos suspended in water is poured into the crucible, the air exhausted from the receiving vessel, and thus a firm thin layer of asbestos is deposited on the bottom of the crucible. After ignition and weighing, the crucible is ready for the reception of any precipitate which it is desired to separate and weigh.

The use of these two pieces of apparatus will eliminate two grave sources of error, viz., incomplete extraction of soluble matters, and inaccuracies introduced by the use of tared paper filters.

The other necessary apparatus is simple, and includes one or more platinum crucibles and evaporating dishes, accurate burettes and graduated cylinders, a good balance, sensitive to at least .5 milligram, and the ordinary glass and porcelain ware found in all laboratories.

It is assumed that whoever attempts the analysis of a plant is informed as to the normal constituents to be sought, that he has had considerable experience in inorganic analysis, and in the identification of the principal classes of proximate con-

\*In place of the linen and filter paper may be substituted fine brass or platinum wire gauze. Asbestos suspended in water may then be poured in to form a fine felt. The tube can then be dried and weighed, and the amounts extracted may be found by the loss of weight of the tube and substance. A little experimentation will show the operator how to prepare and use the tube. It is but an adaptation of the Gooch's filter here recommended.

†Proc. Amer. Acad. Sci. [13], 342, 1878; New Remedies, [7], 290, Oct. 1878; This Journal, 1, 317.

stituents which he now undertakes to estimate quantitatively. Accordingly tests for identification will not be here presented; they should, however, never be omitted. The necessity of recording in detail all physical and chemical peculiarities, with every weight that is taken, is self-evident.

## A METHOD FOR THE PROXIMATE ANALYSIS OF PLANTS.

### I. *Preparation of Sample.*

The air-dry specimen should be carefully examined, and all extraneous substances removed. The entire sample should then be ground, or beaten in an iron mortar, until it will all pass through a sieve having from forty to sixty meshes to the linear inch. After thoroughly mixing this sample, take of it about one hundred grams, which should be further pulverized until it will all pass through a sieve having from eighty to one hundred meshes to the linear inch. From this smaller portion remove all iron, derived from mill or mortar, by use of a magnet. Then place in a clean dry bottle, which should be labelled and securely corked. This small sample is for the analysis; the larger portion should be reserved for the separation of those proximate principles which seem, from the analysis, to be worthy of more extended investigation.

### II. *Estimation of Moisture.*

Dry rapidly, at 100 to 120°C., two or more grams of the sample; the loss of weight equals moisture, and occasionally a little volatile oil. In some cases it is best to dry at a lower temperature, and at other times the drying should be conducted in a stream of hydrogen or carbonic anhydride.

### III. *Estimation of Ash.*

In a weighed crucible gently ignite two or more grams of the sample until nearly or quite free from carbonaceous matter; the heat should not be permitted to rise above faint redness, or loss of alkaline chlorides may occur. Weigh this residue as *crude ash*, and in it determine:

*a. Amount soluble in Water.*—This portion may contain chlorides, sulphates, phosphates, and carbonates of potassium and sodium, also slight amounts of chlorides and sulphates of calcium and magnesium.

*b. Insoluble in Water; Soluble in dilute Hydrochloric Acid.*—The residue from *a* should be treated with a slight excess of hydrochloric acid, and evaporated in a porcelain dish over a water-bath until all free acid has been expelled; it should then be again moistened with hydrochloric acid, water added, and be filtered from any remaining insoluble substances. This treatment removes carbonates (with decomposition) and phosphates of calcium and magnesium, sulphate of calcium, and oxides of iron and manganese.

*c. Insoluble in Water; Insoluble in dilute Hydrochloric Acid; Soluble in concentrated Sodid Hydrate.*—Boil the residue from *b* with a solution containing about twenty per cent. of sodic hydrate. This treatment removes combined silica of the ash. The residue still insoluble is sand and clay which adhered to the specimen; this residue should be separated, washed thoroughly, and weighed.

Always determine the amounts removed by the above treatment by weighing the dried, undissolved residues. The ash, as thus estimated, usually includes a little unconsumed carbon, together with more or less carbonic anhydride ( $\text{CO}_2$ ), most, or all, of which was not originally present in the plant, but was produced by the combustion of the organic matter. For most purposes it is unnecessary to estimate and exclude from the ash this carbonic anhydride; where great accuracy is desired, a complete quantitative analysis should be made, the amount of each base and acid being determined, and in the statement of results only those should be included which existed originally in the plant. For this purpose it is necessary to burn from twenty to one hundred grams of the sample; for further directions consult text-books on agricultural and inorganic analysis.

#### IV. Estimation of Total Nitrogen.

In half a gram or more of the sample determine total nitrogen by combustion with excess of soda-lime, as directed by Prof. S. W. Johnson and E. H. Jenkins.\* If later in the analysis no other nitrogenous substances are discovered, calculate the total amount of nitrogen to albuminoids by multiplying by 6.25. When other nitrogenous compounds are present, their

\* Report Conn. Agric. Exp. Station, 1878; Chem. News, July 18, 1879, p. 28; This Journal, 1, p. 77.

content of nitrogen should be determined directly or by difference ; after proper deductions have been made, the remaining nitrogen should be calculated to albuminoids.

#### V. *Estimation of Benzole Extract.*

In a suitable apparatus for repercolation completely exhaust 5 grams of the sample with pure coal-tar benzole (sp. gr. .85-.88, boils at 80-85° C, leaves no residue when evaporated). The extraction requires from four to six hours' continued action of the solvent. Carefully evaporate this liquid to dryness in a weighed dish, and record its weight as *total benzole extract*. This extract may contain volatile oils and other aromatic compounds, resins, camphors, volatile or non-volatile organic acids, wax, solid fats, fixed oils, chlorophyll, other colors, volatile or fixed alkaloids, glucosides, almost no ash.

To the weighed extract add water, again evaporate on the water-bath, and complete the drying in an air-bath at 110°C. In absence of other vaporizable substances the loss of weight approximates the amount of *volatile oil*. If the presence of a volatile alkaloid is suspected (from a characteristic odor or an alkaline reaction), add a drop of hydrochloric acid to prevent its volatilization. Camphors are partially dissipated by this treatment ; hence, when they are present, this evaporation should be dispensed with.

Treat, now, the residue with a moderate amount of warm water, allow to stand until cool, then filter through fine paper by aid of a Bunsen's pump. In half of the aqueous filtrate determine *total organic matter* and *ash* ; test the remaining half for *alkaloids*, *glucosides*, and *organic acids* by salts of lead, silver, barium and calcium. Care must be taken not to mistake a slight amount of suspended matter, frequently resinous, for other substances actually soluble in water.

The still undissolved residue should be again removed from filters and dishes by solution in benzole, the benzole solution being again evaporated to dryness. Treat this residue with warm, very dilute hydrochloric acid, allow to cool, and filter through paper. The filtrate should be tested for *alkaloids* and *glucosides*. The amount extracted by acid, if any, may be determined by weighing the still undissolved residue. Treat this residue with several considerable portions of eighty per

cent. alcohol (sp. gr. .8483 at 15.6°C.), allowing at least an hour for each treatment. Filter through paper and determine by evaporation the matter dissolved; this usually consists of *chlorophyll* with one or more *resins*, which may sometimes be separated by use of petroleum naphtha, chloroform, or similar solvents. Purified animal charcoal removes *chlorophyll* and *some resins* from alcoholic solution, while certain other resins are not removed. If *camphors* were present in the plant the greater portion will be found in the alcoholic liquid.

The substances undissolved by eighty per cent. alcohol may be *fixed oil*, *solid fat*, *wax*, and very rarely a *resin*: their separation may be attempted by refrigeration and pressure, or by use of ether, chloroform, etc.

### Recapitulation.

1. Loss by evaporation, with precautions: *volatile oil*.
2. Soluble in water: *alkaloids*, *glucosides*, *organic acids*.
3. { Insoluble in water.  
Soluble in dilute acids. } : *Alkaloids*, possibly *glucosides*.
4. { Insoluble in water.  
Insoluble in dilute acids.  
Soluble in 80 per cent. alcohol. } : { a. { Removed by animal charcoal:  
*chlorophyll*, *some resins*.  
b. { Not removed by animal charcoal:  
*some resins*.
5. { Insoluble in water.  
Insoluble in dilute acids.  
Insoluble in 80 per cent. alcohol. } : *wax*, *fats*, *fixed oils*.

It is frequently advantageous to extract the plant with petroleum naphtha (sp. gr. .66-.70, boils at about 50°C., wholly volatile) before treatment with benzole; by reference to the accompanying table of comparative solubilities it will be seen that this treatment may serve to separate fixed and volatile oils and some resins and colors, from certain solid fats, wax, other resins and colors.

Where benzole of sufficient purity cannot be had, pure chloroform is the best substitute. The use of ether is objectionable in this place, as its solvent properties are less distinctly marked than are those of naphtha, chloroform and benzole; in other words, more plant constituents are sparingly

TABLE OF COMPARATIVE SOLUBILITIES.

Substances.	Water.	Ab. Alcohol.	80 per ct. Alcohol.	Ab. Ether.	Chloroform.	Benzole.	Pet. Naph.	10 per ct. Ammonia.	Ammonic Cupric Oxide.	H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O. Sp. gr. 1.78.	Fehling's Sol.	Lead Subacetate.
Volatile oils.....	Sp	Sol	Sol	Sol	Sol	Sol	Sol	Sol	...	...	.....	....
Fixed oils.....	Ins	Ins?	Ins	Ins	Sol	Sol	Sol	Sol?	...	...	.....	....
Wax.....	Ins	Sp	Sp	Sp	Sol	Sol	Sp?	Ins?	...	...	.....	....
Solid fats.....	Ins	Sp	Sp	Sp	Sol	Sol	Sol?	Ins?	...	...	.....	....
Chlorophyll.....	Ins	Sol	Sol	Sol	Sol	Sol	Sol	Ins?	...	...	.....	....
Soft resins.....	Ins	Sol?	Sol	Sol	Sol	Sol	Sol	Ins?	...	...	.....	....
Hard resins.....	Ins	Sol?	Sol	Sol	Sol	Sol	Sol	Sol?	...	...	.....	....
Glucose.....	Sol	Ins	Sp	Ins	Ins	Ins	Ins	Sol	...	...	.....	....
Sucrose.....	Sol	Ins	Sp	Ins	Ins	Ins	Ins	Sol	...	...	Reduced	Not prec
Tannin.....	Sol	Sol	Sol	Sp	Ins	Ins	Ins	Sol	...	...	Not reduced†	Not prec
Glucosides.....	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol	...	...	Reduced	Prec
Alkaloids.....	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	Sol?	...	...	Reduced†	Not prec
Albuminoids.....	Sol?	Sol?	Sol?	Ins	Ins	Ins	Ins	Ins?	...	...	.....	Not prec
Gums.....	Sol	Ins	Ins	Ins	Ins	Ins	Ins	Sol?	...	...	.....	Prec
Pectin.....	Sol	Ins	Ins	Ins	Ins	Ins	Ins	Sol?	...	...	Not reduced	Prec
Pectic acid.....	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Sol	...	...	.....	Prec
Organic acids.....	Sol?	Sol?	Sol	Ins?	Ins?	Ins?	Ins?	Sol	...	...	.....	Prec?
Salts of org. acids..	Sol?	Sol?	Sol?	Ins?	Ins?	Ins?	Ins?	Sol?	...	...	.....	Prec?
Starch.....	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	...	...	.....	....
Cellulose.....	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	...	...	.....	....
"Para cellulose"....	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins*	...	...	.....	....
"Meta cellulose"....	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	...	...	.....	....
"Vasculose".....	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	...	...	.....	....
"Extractives".....	Sol	Ins?	Sol?	Ins	Ins	Ins	Ins	Ins	...	...	Reduced?	Not prec?
Colors.....	Sol?	Ins?	Sol?	Ins	Ins	Ins	Ins	Sol?	...	...	.....	Prec?

\* "Para cellulose" soluble, in ammonia-cupric oxide after boiling with dilute HCl.

† Glucosides reduce Fehling's solution after boiling with dilute acids; same with sucrose.

An ? shows that some marked variations or exceptions occur.

Sp = sparingly soluble. Sol = soluble. Ins = insoluble.

soluble in ether than in the above mentioned solvents. Consequently many substances which should properly be extracted by 80 per cent. alcohol, would be sparingly dissolved if ether were used, while benzole, chloroform, and naphtha would have no perceptible solvent action upon them; tannic acids may be cited as instances illustrating this point.

#### VI. *Estimation of Eighty per cent. Alcohol Extract.*

That part of the plant not dissolved by benzole should be dried at 100°C. and then completely exhausted by eighty per cent. alcohol (sp. gr. .8483 at 15.6°C.). This requires from twelve to fourteen hours' continuous treatment with the solvent. Remove, dry, and weigh any crystals or powder that may separate upon concentrating and cooling the alcoholic percolate. Make the clear liquid to a definite volume by adding more eighty per cent. alcohol. In an aliquot part of this liquid determine *total organic matter* and *ash*: in another equal portion determine *total organic matter* and *ash soluble in water*, and, by difference, *total organic matter insoluble in water*.

The remaining clear alcoholic liquid should be evaporated carefully to dryness, pulverized, and treated with several considerable portions of absolute alcohol (sp. gr. .7938 at 15.6°C.).

#### A. SOLUBLE IN ABSOLUTE ALCOHOL.

##### *a. Soluble in water.*

##### *a<sup>1</sup>. Precipitated by subacetate of lead.*

Tannin and most organic acids; some extractives; some inorganic acids of the ash. Weigh in Gooch's filter, ignite cautiously, and again weigh; loss equals organic matter precipitated.

##### *a<sup>2</sup>. Not precipitated by subacetate of lead.*

Alkaloids, glucosides, some extractives and colors. Determine by difference between *a* and *a<sup>1</sup>*.

##### *b. Insoluble in water.*

##### *b<sup>1</sup>. Soluble in dilute hydrochloric acid.*

Alkaloids, glucosides (rarely), some extractives. Determine by difference between *b* and *b<sup>2</sup>*.

##### *b<sup>2</sup>. Insoluble in dilute hydrochloric acid.*

*b*<sup>3</sup>. Soluble in dilute ammoniac hydrate.

Most acid resins, some colors. Determine by difference between *b*<sup>2</sup> and *b*<sup>4</sup>.

*b*<sup>4</sup>. Insoluble in dilute ammoniac hydrate.

Neutral resins, some colors, albuminoids (in some seeds). Redissolve in alcohol, evaporate and weigh.

## B. INSOLUBLE IN ABSOLUTE ALCOHOL.

*c*. Soluble in water.

*c*<sup>1</sup>. Precipitated by subacetate of lead.

Some colors, extractives, albuminoids (rarely), organic acids, and inorganic acids of the ash. Weigh in Gooch's filter, ignite cautiously, and again weigh; loss equals organic matter precipitated.

*c*<sup>2</sup>. Not precipitated by subacetate of lead.

Alkaloids, glucosides, sucrose, glucose, some extractives. Determine by difference between *c* and *c*<sup>1</sup>. Remove Pb by H<sub>2</sub>S, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, or other means, and titrate for sucrose and glucose.

*d*. Insoluble in water.

*d*<sup>1</sup>. Soluble in dilute hydrochloric acid.

Some alkaloids and glucosides. Determine by difference between *d* and *d*<sup>2</sup>.

*d*<sup>2</sup>. Insoluble in dilute hydrochloric acid.

Few resins, some extractives, and color substances. Dissolve in alcohol, evaporate and weigh in a tared dish.

In some cases it may be preferable to use the following method for analysis of the eighty per cent. alcohol extract; it is more desirable when the plant examined contains a considerable amount of sugars, tannic acid, etc.

*Alcohol Extract*, dilute to 200 c. c. with eighty per cent. alcohol.

1. In 20 c. c. determine *total organic matter* and *ash*.

2. In 20 c. c. determine *total organic matter* and *ash* that are *soluble in water*, and, by difference, *total organic matter insoluble in water*.

3. Evaporate the remaining 160 c. c. to dryness, treat with water, filter, and make the filtrate measure 160 c. c. Reserve the insoluble matter on the filter for examination. (10).

4. In 20 c. c. of the aqueous solution determine tannin gravimetrically by A. Carpeni's method;\* precipitate by ammoniacal acetate of zinc, use a Gooch's filter, wash the precipitate with very weak ammonia, dry at 120°C., weigh, ignite cautiously, again weigh. The loss by ignition equals tannic acid, in absence of certain interfering substances.

5. Precipitate 20 c. c. by normal acetate of lead, and determine, as before described, the amount of organic matter after drying at 100–120°C. This precipitate will contain, if the substances are present in the plant, *tannic*, *gallic*, and most other *organic acids*, some *colors*, rarely *albuminous substances*, some *extractives*, and most *inorganic acids* of the ash. Determine, by difference, the amount not precipitated by this treatment.

6. In 20 c. c. determine in like manner the amount precipitated by basic acetate ("subacetate") of lead. This reagent precipitates a greater number of acids, colors and extractives than are precipitated by the normal acetate, hence it is frequently possible to estimate such substances by subtracting the amount precipitated by one reagent from the amount precipitated by the other. To the filtrate add a slight excess of dilute hydrochloric acid, boil gently for half an hour, and determine in the liquid *total glucose* by use of Fehling's solution.

7. Precipitate 20 c. c. by subacetate, exactly as in 6, and use the precipitate as a duplicate to check the amount there estimated. To the filtrate add a very slight excess of solution of carbonate of sodium, filter from the carbonate of lead, wash well with water containing a little alcohol, and in the filtrate estimate *actual glucose*. If the glucose thus found is appreciably less than that in 6, subtract it from that amount; this glucose may be due to the presence in the plant of *sucrose* or some *glucoside*. If due to *sucrose*, the amount of the latter may be found by multiplying this residual glucose by .95; if to a *glucoside*, a fit subject for an extended investigation is presented. The properties, formula, and decomposition products of the newly-found glucoside should be carefully studied.

8. Precipitate 20 c. c. with subacetate of lead, as in 6 and 7, employing the precipitate as material from which to separate

\* Chem. News, July 9, 1875, p. 19, from Gaz. Chim. Ital. 1875, No. 3; Proc. Am. Ph. Assn. 1875, p. 341.

organic acids, after removal of lead by sulphuretted hydrogen. Acidulate the filtrate with sulphuric acid, add an equal volume of alcohol, allow to stand two hours, filter, wash the precipitate with fifty per cent. alcohol, and evaporate the filtrate until all alcohol has been dissipated. Test the acid solution for *alkaloids, glucosides, sugars, extractives*.

9. Reserve the remaining 40 c. c. for duplicating any unsatisfactory determinations.

10. The residue mentioned in 3 as insoluble in water may contain *resins, albuminoids* (especially from seeds), *colors, alkaloids, glucosides*. Dilute acids remove *alkaloids* and some *glucosides*, dilute ammoniac hydrate will remove some *resins, colors, and glucosides*. Any still insoluble residue probably contains *albuminous or resinous* substances.

#### VII. *Estimation of Cold Water Extract.*

That part of the plant remaining insoluble after treatment with alcohol should be dried at 110°C. and completely extracted by cold water. When the plant contains considerable mucilaginous matter, this is best removed by placing the substance in a flask or graduated cylinder, and then adding a measured volume of cold water. Allow to macerate, with frequent agitation, for from six to twelve hours; then filter through fine washed linen, and evaporate an aliquot portion of the solution. In this residue determine *total organic matter* and *ash*. This residue usually contains little but *gum*; in analysis of fruits and fleshy roots *pectin bodies, salts of organic acids*, rarely a substance resembling *dextrin*, and small amounts of *albuminous substances* and *coloring matter*. Usually the separation of these substances is very difficult. The unevaporated liquid should be used for such qualitative reactions as are necessary to show the nature of the substances extracted. The insoluble residue should be well washed with water, transferred to a crucible, and completely dried at 110°C. This residue should be then weighed.

#### VIII. *Estimation of Acid Extracts.*

The dried residue insoluble in cold water should be transferred to a beaker containing 500 c. c. of water and 5 c. c. of

concentrated sulphuric acid (sp. gr. 1.84). Boil for six hours, on a gauze support, adding water to keep the volume of liquid unchanged; if the substance be very starchy, a longer boiling may be necessary. This treatment will convert *starch* and its *amorphous isomers* to dextro-glucose, and will occasionally remove some *salt of an organic acid*, with usually traces of *albuminous* and *indeterminate* substances.

The *total amount extracted* may be found by washing, drying at  $110^{\circ}\text{C}$ ., and weighing the yet insoluble residue, and subtracting the weight from the one taken after extracting with cold water. The amount of *starch and isomers* may be found by determining in a given volume of the acid filtrate the amount of *glucose*, using Fehling's solution; the glucose thus found multiplied by .9 equals starch and isomers. The *total extract* minus *starch and isomers* equals *acid extract not starch*. This includes a small amount of *ash*, which may be approximately determined by evaporating and igniting a known volume of the solution.

Where it is wished to separate the extracted matter from the sulphuric acid, boil the liquid with an excess of powdered barium carbonate until no acid reaction remains. Filter, and evaporate to dryness. The residue consists chiefly of hydrated dextro-glucose ( $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ ), with some ash.

### IX. Estimation of Alkali Extract.

Wash well and dry at  $110^{\circ}\text{C}$ . the residue from treatment with acid, and record its weight. Boil this residue, for two hours, with 500 c.c. of a solution containing 20 grams of sodic hydrate to the litre. Filter through fine washed linen, and wash the residue thoroughly with hot water, alcohol and ether. Transfer it to a weighed crucible, dry at  $110\text{-}120^{\circ}\text{C}$ ., and weigh the residue as *crude fibre* and *ash*; this weight subtracted from the previous one shows the *total alkali extract*. This extract is largely *albuminous matter* and various modifications of *pectic acid*, Fremy's "*cutose*," and various *coloring*, *humus*, and *decomposition compounds* in small amounts. Most of the extracted substances may be precipitated by excess of an acid with or without the presence of alcohol.

X. *Cellulose.*

The crude fibre from IX should be treated with from 50 to 100 c.c. of U. S. P. solution of chlorinated soda and allowed to stand twenty-four hours. If not then bleached white, slightly acidulate with hydrochloric acid, and set aside for another day. Filter through fine linen, or Gooch's filter, wash with hot water, dry at 110-120°C., and weigh, ash free, as *cellulose*. The loss of weight by this treatment state as *lignose* and *color*.

*Remarks.*

It is advisable to determine always, in addition to what has already been directed, the amounts extracted directly from the sample by water, ether, alcohol of various percentages, methylic alcohol, naphtha, chloroform, carbon disulphide, etc. In each extract estimate *total organic matter* and *ash*, determine qualitatively, and quantitatively when possible, its constituents, by treating with such solvents and reagents as are indicated. Each extract being composed of certain distinct substances, it is necessary to account for them in every case.

The amounts present of some constituents may be found by subtracting the weight extracted by some one solvent from the weight extracted by some other. It will be seen that this is a method of limited applicability, which can only be applied in those cases where the difference between the solvent action of the two liquids is very sharply defined. Certain special methods for the estimation of single constituents may be used, care being taken that all interfering substances be first removed. The methods of preparation of known substances as given in Husemann's *Pflanzenstoffe*, and to a considerable extent in Watt's *Dictionary*, may serve as suggestions for work. Treatment with benzole, eighty per cent. alcohol, and water, removes from nearly all plants the constituents of greatest chemical and medicinal interest, but in analyses of grains, fodder, and food materials those compounds extracted by dilute acids and alkalis have great value. There are substances in plants, seemingly isomers of starch and cellulose, which have properties more or less resembling those of cellulose, and are changed by boiling with dilute acids to glucose. In absence of an established nomenclature it has seemed best

to use the terms "starch isomers," or "amylaceous cellulose" for these substances,\* while those constituents, *not albuminous*, which are not removed by dilute alkali have been termed "alkali extract." These substances have been investigated by various chemists, but no definite and authoritative nomenclature has yet been adopted. Thomsen gives the name "holz-gummi",† *wood-gum*, to a white substance extracted from plants by dilute sodic hydrate, while Fremy regards these various compounds as modifications of pectic acid, pectin, and "cellulose bodies."‡ Starch also may exist in some seeds (as of sweet corn) in a form soluble in water.§

It will be seen that the field for investigation is limitless, and almost unoccupied as yet, and that there is great need for improved methods for proximate analysis. The analyst will find that a study of any common plant will require of him much more than unthinking, mechanical habits of manipulation, while every careful investigation will reveal to him some constituents deserving more full and accurate study.

WASHINGTON, D. C., Nov. 26th, 1879.

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## ON THE ESTIMATION OF PHOSPHORIC ACID AS MAGNESIC PYROPHOSPHATE.||

BY F. A. GOOCH.

The investigation of which this paper is an account, was undertaken at the request of Dr. Wolcott Gibbs, for the purpose of finding, for use in his work upon the complex inorganic acids, the best mode of proceeding in determining the phosphoric oxide of phosphotungstates and phosphomolybdates by precipitation as ammonio-magnesian phosphate and estimation as magnesian pyrophosphate. During the course of

\* U. S. Dept. of Agric. Report, 1878, p. 180.

† Kolbe's Jour. Prak. Chem. Band 19, p. 146.

‡ Compt. rend. lxxxiii. 1136; Jour. Ch. Soc. 1877, p. 229.

§ U. S. Dept. of Agric. Report, 1878, pp. 153-155.

|| Presented to the American Academy of Arts and Sciences. Communicated by the Author.

the work it has been found necessary to review much of what has been previously published concerning this method of determining phosphoric acid.

In a paper upon this subject, Kubel\* criticised Fresenius's correction † (subsequently withdrawn ‡) for the solubility of ammonio-magnesian phosphate in water containing free ammonia and magnesia mixture, and asserted that such correction is not only unnecessary, but that the results of the analysis are of themselves much higher than theory indicates, unless the precipitate is, after washing, dissolved and reprecipitated. Kubel's method was to add hydrochloric acid and then ammonia, or ammoniac chloride, or ammonia, to a measured amount of a solution of sodic phosphate, to precipitate with magnesian sulphate mixture, and after twelve hours to filter off and wash with dilute ammonia containing one part of strong ammonia to three of water. A number of analyses made in this way gave amounts of phosphoric oxide varying from 101.5 to 104.3 per cent. of the real quantity present,—the actual weight being in each case 0.1986 gr. Another set of analyses in which the precipitate was, after washing, dissolved in hydrochloric acid and again thrown down with ammonia, but which were otherwise treated in the same manner as the first, gave figures for phosphoric oxide varying from 99.8 per cent. to 100.5 per cent. of the real amount. When the precipitate was twice dissolved and twice reprecipitated, the amount of phosphoric oxide indicated was 99.8 per cent., and when three times dissolved and reprecipitated, 99.2 per cent. of the real amount. While noting that the precipitate is not absolutely insoluble in ammonia, more especially if it contain ammoniac chloride, Kubel concludes, supposing that a basic sulphate or hydrate of magnesium is thrown down with the first precipitate, that this precipitate must be dissolved after washing and again thrown down with ammonia.

Kissel,§ by using large amounts of ammoniac chloride, washing copiously in order to make the solubility of the precipitate compensate for the inclusion of foreign matter, and taking care to use no great excess of the magnesian sulphate mixture, obtains in one set of experiments from 99.4 to 99.6

\* Zeitschrift f. anal. Chem. VIII. 125.

† Ibid. 6 Aufl. 184.

‡ Anleitung zur Quant. Anal. 5 Aufl. 333.

§ Zeitschrift f. anal. Chem. VIII. 169.

per cent., in another from 99.8 to 100 per cent., of the correct amount of phosphoric oxide. Of three filtrates from the precipitated ammonio-magnesian phosphate, two gave weak reactions for phosphoric acid with acid ammonic molybdate, and one no reaction. The wash-water tested by the same method gave in every case a plain reaction. Heintz\* supports Kubel so far as to say that in presence of any considerable excess of magnesian sulphate mixture the precipitate must be dissolved after incomplete washing. Brunner† points out that the solution must not be precipitated hot by magnesian sulphate mixture on account of the danger of throwing down magnesian hydrate. Schumann‡ supports Kissel in the view that the solution of the first precipitate is unnecessary, but adds a caution against the addition of ammonia after the magnesian sulphate mixture.

Finally, Abesser, Jani, and Mærcker§ substantiate Kubel's results, and having proved the presence of a sulphate in the precipitate, obtain somewhat better figures by igniting over the blast. Adopting the method of precipitating by magnesian chloride mixture previously suggested by Brassier|| and Bunsen,¶ and recommended in the works of Rose\*\* and Fresenius,†† their analyses show from 99.96 per cent. to 100.48 per cent. of the true amount of phosphoric oxide. The weight of phosphoric oxide used in each of their experiments was not far from 0.1250 gr. The precipitate was washed until the reaction for chlorine with argentic nitrate failed to appear in the filtrate acidified with nitric acid. The method of precipitating with magnesian chloride and igniting over the Bunsen lamp, gave in their hands from 99.96 to 100.48 per cent.; the method of precipitating with magnesian sulphate and igniting over the blast, from 100.4 to 100.7 per cent.; and the method of precipitating with magnesian sulphate and igniting over the Bunsen lamp, from 101.4 to 103.1 per cent. of the actual amount of phosphoric oxide.

All agree that the precipitated ammonio-magnesian phosphate is soluble to a very considerable extent in dilute ammonia, and to a greater extent in ammonia containing ammoniac

\* *Zeitsch. f. anal. Chem.* IX. 16. + *Ibid.* XI. 20. † *Ibid.* XI. 382. § *Ibid.* XII. 239.

|| *Ann. de Chim. et de Phys.* [4] VII. 335. ¶ *Zeitschrift f. anal. Chem.* X. 305.

\*\* *Rose's analytische Chemie*, VI. Aufl., 512, bearbeitet von Finkener.

†† *Anleit. zur Quant. Anal.*, 6 Aufl., 403.

chloride; that the presence of a magnesia salt tends to prevent the solution of the precipitate; and that when magnesian sulphate is used in excess as a precipitant, the precipitate includes, mechanically or otherwise, an appreciable amount of magnesian sulphate, or magnesian hydrate, or both. Kissel and Schumann aim to arrive at correct results by precipitating with as little excess of magnesian sulphate mixture as possible, and compensating for foreign inclusions by dissolving a part of the precipitate. Kubel and Heintz strive to reach the same end by removing the excess of the precipitant, together with the included impurity, by filtering off, dissolving, and again throwing down the precipitate.

With this preface, I proceed to the description of my own experiments upon this subject.

I have worked with measured portions of solutions of hydro-sodic phosphate, or of microcosmic salt, the standards of which were, in all cases but one, determined by evaporating a known volume to dryness, igniting the residue and weighing the remaining sodic pyrophosphate or metaphosphate as the case might be. In the one exceptional case, a known weight of microcosmic salt, freshly crystallized and dried, the volatile constituents of which had been determined by igniting separate portions, was dissolved in a known volume of water. The experiments which fixed the standards of these solutions are given below.

I. Two portions of 20 cm.<sup>3</sup> each of a solution of hydro-sodic phosphate were evaporated to dryness, and the residue was ignited and weighed as sodic pyrophosphate.

(1) gave of  $\text{Na}_4\text{P}_2\text{O}_7$  0.1217 gr.

(2) “ “ 0.1214 gr.

The solution contained, therefore, 0.1298 gr. of  $\text{P}_2\text{O}_5$  to every 40 cm.<sup>3</sup>

II. A quantity of microcosmic salt was recrystallized, dried between papers by pressure, and the amount of loss on ignition determined in two portions.

(1) 1.1419 gr. gave of  $\text{NaPO}_3$  0.5836 gr. = 51.11 per ct.

(2) 0.9846 gr. “ “ 0.5027 gr. = 51.06 per ct.

Of this salt 3.7583 gr. were dissolved in water and the solution diluted to one litre. The solution contained, therefore, 0.0512 gr. of  $\text{P}_2\text{O}_5$  to every 40 cm.<sup>3</sup>

III. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3490 gr.

(2) " " " " 0.3490 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1863 gr.  $\text{P}_2\text{O}_5$ .

IV. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3530 gr.

(2) " " " " 0.3533 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1885 gr.  $\text{P}_2\text{O}_5$ .

V. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3512 gr.

(2) " " " " 0.3514 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1875 gr.  $\text{P}_2\text{O}_5$ .

VI. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.4112 gr.

(2) " " " " 0.4113 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.2195 gr.  $\text{P}_2\text{O}_5$ .

VII. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 40 cm.<sup>3</sup> 0.3429 gr.

(2) " " " " 0.3429 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.1831 gr.  $\text{P}_2\text{O}_5$ .

VIII. The solution contained microcosmic salt.

(1) gave  $\text{NaPO}_3$  from 40 cm.<sup>3</sup> 0.3077 gr.

(2) " " " " 0.3078 gr.

Every 40 cm.<sup>3</sup>, therefore, contained 0.2142  $\text{P}_2\text{O}_5$ .

IX. The solution contained microcosmic salt.

(1) gave  $\text{NaPO}_3$  from 40 cm.<sup>3</sup> 0.2897 gr.

(2) " " " " 0.2900 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.2017 gr.  $\text{P}_2\text{O}_5$ .

X. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 20 cm.<sup>3</sup> 0.0247 gr.

(2) " " " " 0.0249 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.0265 gr.  $\text{P}_2\text{O}_5$ .

XI. The solution contained hydro-disodic phosphate.

(1) gave  $\text{Na}_4\text{P}_2\text{O}_7$  from 20 cm.<sup>3</sup> 0.0249 gr.

(2) " " " " 0.0250 gr.

Every 40 cm.<sup>3</sup> contained, therefore, 0.0266 gr.  $\text{P}_2\text{O}_5$ .

XII. The solution consisted of 71.5 cm.<sup>3</sup> of Solution IV. diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0270 gr.  $\text{P}_2\text{O}_5$ .

XIII. The solution consisted of 71.5 cm.<sup>3</sup> of Solution IV.

diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0270 gr.  $P_2O_5$ .

XIV. The solution consisted of 61.3 cm.<sup>3</sup> of Solution VI. diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0269 gr.  $P_2O_5$ .

XV. The solution consisted of 61.3 cm.<sup>3</sup> of Solution VI. diluted to 500 cm.<sup>3</sup> Every 40 cm.<sup>3</sup> contained, therefore, 0.0269 gr.  $P_2O_5$ .

XVI. The solution consisted of 125.6 cm.<sup>3</sup> of Solution VIII. diluted to one litre. Every 40 cm.<sup>3</sup> contained, therefore, 0.0269 gr.  $P_2O_5$ .

Each of the following experiments was made with 40 cm.<sup>3</sup> of another of these solutions diluted (if necessary), so that the volume after precipitation should for the weaker solutions be about 100 cm.<sup>3</sup>, and for the stronger solutions from 125 cm.<sup>3</sup> to 150 cm.<sup>3</sup>

Precipitation was effected in cold solutions unless the contrary is stated, and, when not otherwise specified, either by a magnesian sulphate mixture consisting of one part of crystallized magnesian sulphate, two of ammoniac chloride, four of concentrated ammonia, and eight of water; or by a magnesian chloride mixture containing three parts of crystallized magnesian chloride, eight of ammoniac chloride, sixteen of concentrated ammonia, and thirty-two of water. The precipitate of ammonio-magnesian phosphate was, in every case, finally collected on asbestos felt in a perforated platinum crucible according to the process previously described by me,\* washed with 60 cm.<sup>3</sup> to 70 cm.<sup>3</sup> (applied in successive portions) of a solution of one part of concentrated ammonia to three of water,—this amount being found to be more than sufficient for washing, when the asbestos process is used, until the filtrate ceases to show the presence of chlorine when treated with nitric acid and argentic nitrate,—moistened with a few drops of a solution of ammoniac nitrate in ammonia, dried on the vacuum pump, ignited on a platinum crucible-cover, at first gently until fumes of ammoniac nitrate no longer appeared, then at a full red heat until the spreading of a glow over the whole residue indicated the formation of the magnesian pyrophosphate.

\* Proceedings Amer. Acad. Arts and Sci. XIII. 342; and This Journal, 1, 317.

The results of the experiments are tabulated below. The figures of the first column show the weights of magnesian pyrophosphate found, those of the second the corresponding weights of phosphoric oxide, those of the third the weight of phosphoric oxide required by the determinations of the standard of the solution used, those of the fourth the absolute error in the determination of phosphoric oxide, and those of the fifth the percentage error referred to the actual amount of phosphoric oxide present. The Roman numeral standing against the record of each experiment shows which phosphate solution was used in that experiment.

*Alkaline Phosphates.*

Experiments (1) to (10) inclusive were made with 40 cm.<sup>3</sup> each of the phosphate solution. Portions (1) and (2) were precipitated with 20 cm.<sup>3</sup> of magnesian sulphate mixture. Portions (3) to (6) were treated with 20 cm.<sup>3</sup> of a magnesian sulphate mixture containing only a small amount of free ammonia, but the same weights of magnesium and ammonium salts as the regular mixture. The first precipitates of (3) and (4) were dissolved in hydrochloric acid and again thrown down by ammonia in presence of the excess of the precipitant, and those of (5) and (6) were dissolved and reprecipitated in this manner twice. Portions (7) to (10) were precipitated with 20 cm.<sup>3</sup> of magnesian sulphate mixture after being acidulated—(7) and (8) with hydrochloric acid, (9) and (10) with 0.5 gr. of citric acid—and made alkaline with ammonia.

	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
I.	(1) 0.2082 gr.	0.1331 gr.	0.1298 gr.	+ 0.0033 gr.	+ 2.54
	(2) 0.2113 gr.	0.1352 gr.	0.1298 gr.	+ 0.0054 gr.	+ 4.16
	(3) 0.2104 gr.	0.1346 gr.	0.1298 gr.	+ 0.0048 gr.	+ 3.70
	(4) 0.2124 gr.	0.1358 gr.	0.1298 gr.	+ 0.0060 gr.	+ 4.62
	(5) 0.2095 gr.	0.1340 gr.	0.1298 gr.	+ 0.0042 gr.	+ 3.23
	(6) 0.2097 gr.	0.1342 gr.	0.1298 gr.	+ 0.0044 gr.	+ 3.39
X.	(7) 0.0420 gr.	0.0269 gr.	0.0265 gr.	+ 0.0004 gr.	+ 1.51
	(8) 0.0427 gr.	0.0273 gr.	0.0265 gr.	+ 0.0008 gr.	+ 3.02
	(9) 0.0444 gr.	0.0284 gr.	0.0265 gr.	+ 0.0019 gr.	+ 7.17
	(10) 0.0448 gr.	0.0286 gr.	0.0265 gr.	+ 0.0021 gr.	+ 7.92

Experiments (11) to (16) inclusive were made with portions of 40 cm.<sup>3</sup> each of Solution II. Portions (11) and (12) were acidulated with hydrochloric acid and, after the addition of ammonia in excess, precipitated with 6 cm.<sup>3</sup> of magnesian sulphate mixture. Portions (13) and (14) were acidulated with 0.5 gr. of citric acid and, after the addition of ammonia, treated with 6 cm.<sup>3</sup> of magnesian sulphate mixture; which amount failing (on account of the presence of a citrate) to throw the phosphoric acid down entirely, 6 cm.<sup>3</sup> more of the same mixture were added to complete the precipitation. Portions (15) and (16) were acidulated with hydrochloric acid and 0.5 gr. of citric acid, ammonia added in excess and precipitation effected with 12 cm.<sup>3</sup> of magnesian sulphate mixture. The precipitates of (11), (13), and (15) were filtered off, washed and ignited; those of (12), (14), and (16) were filtered off on paper, drained, dissolved (without previous washing) in hydrochloric acid, thrown down again with ammonia, and, the precipitate having settled, filtered off, after the addition of a few centimetres of magnesian sulphate mixture, upon asbestos, washed and ignited. The precipitates were all thrown down the first time from hot solutions.

	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
II.	(11) 0.0811 gr.	0.0519 gr.	0.0512 gr.	+ 0.0007 gr.	+ 1.37
	(12) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(13) 0.0827 gr.	0.0529 gr.	0.0512 gr.	+ 0.0017 gr.	+ 3.31
	(14) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.
	(15) 0.0827 gr.	0.0529 gr.	0.0512 gr.	+ 0.0017 gr.	+ 3.31
	(16) 0.0801 gr.	0.0512 gr.	0.0512 gr.	0.	0.

Experiments (17) to (20) inclusive were made with portions of 40 cm.<sup>3</sup> each of Solution III. To each portion were added 6 cm.<sup>3</sup> of strong hydrochloric acid, 20 cm.<sup>3</sup> of strong ammonia, and 20 cm.<sup>3</sup> of magnesian sulphate mixture. The first precipitate was filtered off on paper, drained, dissolved in hydrochloric acid and thrown down again with ammonia. In portions (17) and (18) the second precipitation was effected instantly by adding concentrated ammonia to the acid solution, the precipitate being consequently quite voluminous, and magnesian sulphate mixture was added after settling. In portions (19) and (20) the second precipitation was brought about more gradually by neutralizing with dilute ammonia.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.	
III.	{	(17)	0.2928 gr.	0.1873 gr.	0.1863 gr.	+ 0.0010 gr.	+ 0.54
		(18)	0.2937 gr.	0.1878 gr.	0.1863 gr.	+ 0.0015 gr.	+ 0.80
		(19)	0.2923 gr.	0.1869 gr.	0.1863 gr.	+ 0.0006 gr.	+ 0.32
		(20)	0.2925 gr.	0.1871 gr.	0.1863 gr.	+ 0.0008 gr.	+ 0.43

In experiments (21) to (26) inclusive, 40 cm.<sup>3</sup> of magnesian sulphate mixture, from which the ammonia had been removed by boiling, were in each case added to 40 cm.<sup>3</sup> of the phosphate solution; in (21), (22), (23), and (24) directly, in (25) and (26) after acidifying with 5 cm.<sup>3</sup> of strong hydrochloric acid and then making faintly but distinctly ammoniacal. In every case dilute ammonia was added gradually at first, and 5 cm.<sup>3</sup> of strong ammonia after, the settling of the precipitate. Portions (21) and (22) were precipitated hot.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.	
V.	{	(21)	0.3112 gr.	0.1991 gr.	0.1875 gr.	+ 0.0116 gr.	+ 6.18
		(22)	0.3114 gr.	0.1992 gr.	0.1875 gr.	+ 0.0117 gr.	+ 6.24
		(23)	0.3028 gr.	0.1936 gr.	0.1875 gr.	+ 0.0061 gr.	+ 3.25
		(24)	0.3048 gr.	0.1949 gr.	0.1875 gr.	+ 0.0074 gr.	+ 3.94
VIII.		(25)	0.3469 gr.	0.2219 gr.	0.2142 gr.	+ 0.0077 gr.	+ 3.59
		(26)	0.3514 gr.	0.2248 gr.	0.2142 gr.	+ 0.0106 gr.	+ 4.94

For experiments (27) to (39) inclusive portions of 40 cm.<sup>3</sup> each of the phosphate solutions were taken. To portions (27) and (28) were added 12 cm.<sup>3</sup> of magnesian chloride mixture; to (29) and (30) 5 cm.<sup>3</sup> of strong hydrochloric acid, strong ammonia to neutralization and 10 cm.<sup>3</sup> beside, and then 12 cm.<sup>3</sup> of magnesian chloride mixture; to portions (31) to (39) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid, 20 cm.<sup>3</sup> of strong ammonia and 10 cm.<sup>3</sup> of magnesian chloride mixture, 5 cm.<sup>3</sup> more of the same being added, except in experiment (31), after the settling of the precipitate.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.	
VI.	{	(27)	0.3430 gr.	0.2194 gr.	0.2195 gr.	— 0.0001 gr.	— 0.04
		(28)	0.3438 gr.	0.2199 gr.	0.2195 gr.	+ 0.0004 gr.	+ 0.18
		(29)	0.3425 gr.	0.2191 gr.	0.2195 gr.	— 0.0004 gr.	— 0.18
		(30)	0.3435 gr.	0.2197 gr.	0.2195 gr.	+ 0.0002 gr.	+ 0.09

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
III.	{ (31)	0.2902 gr.	0.1857 gr.	0.1863 gr.	— 0.0006 gr.	— 0.32
	{ (32)	0.2903 gr.	0.1857 gr.	0.1863 gr.	— 0.0006 gr.	— 0.32
	{ (33)	0.2908 gr.	0.1860 gr.	0.1863 gr.	— 0.0003 gr.	— 0.16
	{ (34)	0.2913 gr.	0.1863 gr.	0.1863 gr.	0.	0.
	{ (35)	0.2919 gr.	0.1866 gr.	0.1863 gr.	+ 0.0003 gr.	+ 0.16
	{ (36)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+ 0.0004 gr.	+ 0.21
	{ (37)	0.2920 gr.	0.1867 gr.	0.1863 gr.	+ 0.0004 gr.	+ 0.21
IV.	{ (38)	0.2935 gr.	0.1877 gr.	0.1885 gr.	— 0.0008 gr.	— 0.42
	{ (39)	0.2941 gr.	0.1880 gr.	0.1885 gr.	— 0.0005 gr.	— 0.27

In experiments (40) to (43) inclusive 10 cm.<sup>3</sup> of strong ammonia were added to 40 cm.<sup>3</sup> of the phosphate solution and then 10 cm.<sup>3</sup> of magnesian chloride mixture. The precipitates of (42) and (43) were dissolved by adding hydrochloric acid to the supernatant liquid and thrown down again with ammonia.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
V.	{ (40)	0.2946 gr.	0.1884 gr.	0.1875 gr.	+ 0.0009 gr.	+ 0.48
	{ (41)	0.2950 gr.	0.1887 gr.	0.1875 gr.	+ 0.0012 gr.	+ 0.64
	{ (42)	0.2927 gr.	0.1872 gr.	0.1875 gr.	— 0.0003 gr.	— 0.16
	{ (43)	0.2936 gr.	0.1878 gr.	0.1875 gr.	+ 0.0003 gr.	+ 0.16

In experiments (44) to (47) inclusive 10 cm.<sup>3</sup> of strong ammonia were added to 40 cm.<sup>3</sup> of the phosphate solution, and then 25 cm.<sup>3</sup> of magnesian chloride. The precipitates of (46) and (47) were dissolved by hydrochloric acid added to the supernatant liquid and again thrown down with ammonia.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
IV.	{ (44)	0.2977 gr.	0.1904 gr.	0.1885 gr.	+ 0.0019 gr.	+ 1.01
	{ (45)	0.2986 gr.	0.1910 gr.	0.1885 gr.	+ 0.0025 gr.	+ 1.33
	{ (46)	0.2952 gr.	0.1888 gr.	0.1885 gr.	+ 0.0003 gr.	+ 0.16
	{ (47)	0.2954 gr.	0.1889 gr.	0.1885 gr.	+ 0.0004 gr.	+ 0.21

For each of the experiments (48) to (60) inclusive 40 cm.<sup>3</sup> of the phosphate solution were taken. Portions (48), (49), (50) and (51) were precipitated with 40 cm.<sup>3</sup> of magnesian chloride mixture containing 4 gr. of ammoniac chloride more than the usual amount, the precipitant being added to the phosphate in experiments (48) and (49), the phosphate (gradually) to the precipitant in (50) and (51). In experiments (52) and (53) the solution of the phosphate was acidulated with 8 cm.<sup>3</sup> of

hydrochloric acid, made alkaline with ammonia — about 4 gr. of ammonic chloride being produced in the process — and precipitated with 40 cm.<sup>3</sup> of magnesic chloride mixture. In experiments (54) to (60) inclusive 40 cm.<sup>3</sup> of magnesic chloride mixture from which the ammonia had been expelled by boiling were added to the phosphate solution — in experiments (56), (57), (58), (59) and (60) directly, in (54) and (55) after adding enough ammonia to make the solution smell distinctly of it — and ammonia afterward strong in (57), (58), (59) and (60), but dilute at first in (54), (55), and (56) and strong after the settling of the precipitate. Solutions (59) and (60) were precipitated hot.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
VII.	{	(48) 0.2880 gr.	0.1842 gr.	0.1831 gr.	+ 0.0011 gr.	+ 0.60
		(49) 0.2881 gr.	0.1843 gr.	0.1831 gr.	+ 0.0012 gr.	+ 0.66
		(50) 0.2886 gr.	0.1846 gr.	0.1831 gr.	+ 0.0015 gr.	+ 0.82
		(51) 0.2888 gr.	0.1847 gr.	0.1831 gr.	+ 0.0016 gr.	+ 0.87
		(52) 0.2882 gr.	0.1844 gr.	0.1831 gr.	+ 0.0013 gr.	+ 0.71
		(53) 0.2883 gr.	0.1844 gr.	0.1831 gr.	+ 0.0013 gr.	+ 0.71
		(54) 0.2865 gr.	0.1832 gr.	0.1831 gr.	+ 0.0001 gr.	+ 0.05
V.	{	(55) 0.2870 gr.	0.1835 gr.	0.1831 gr.	+ 0.0004 gr.	+ 0.22
		(56) 0.2931 gr.	0.1875 gr.	0.1875 gr.	0.	0.
		(57) 0.2940 gr.	0.1880 gr.	0.1875 gr.	+ 0.0005 gr.	+ 0.27
		(58) 0.2950 gr.	0.1887 gr.	0.1875 gr.	+ 0.0012 gr.	+ 0.64
		(59) 0.2983 gr.	0.1907 gr.	0.1875 gr.	+ 0.0032 gr.	+ 1.70
		(60) 0.3017 gr.	0.1930 gr.	0.1875 gr.	+ 0.0055 gr.	+ 2.93

In experiments (61) to (66) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid were added to 40 cm.<sup>3</sup> of the phosphate solution, and then ammonia in slight excess. Portions (61), (62), (63), and (64), were precipitated with 20 cm.<sup>3</sup> of magnesic chloride mixture. To (65) and (66) were added 20 cm.<sup>3</sup> of magnesic chloride mixture from which the ammonia had been expelled, and afterward ammonia dilute at the first and strong after the precipitate had settled. Solutions (63), (64), (65) and (66) contained previous to precipitating 3 gr. of sodic chloride each.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XVI.	{	(61) 0.0426 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11
		(62) 0.0427 gr.	0.0273 gr.	0.0269 gr.	+ 0.0004 gr.	+ 1.49
		(63) 0.0430 gr.	0.0275 gr.	0.0269 gr.	+ 0.0006 gr.	+ 2.23
		(64) 0.0431 gr.	0.0276 gr.	0.0269 gr.	+ 0.0007 gr.	+ 2.60
		(65) 0.0426 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11
		(66) 0.0426 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11

*Phosphotungstates.*

In each of the following experiments upon the determination of phosphoric oxide in phosphotungstates 1 gr. of crystallized normal sodic tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) was dissolved and added to 40 cm.<sup>3</sup> of a phosphate solution, the phosphotungstate produced by the addition of acid in measured amount or until the yellow color of the solution indicated its formation, and ammonia added until the precipitate first formed redissolved.

In experiments (67) to (76) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid, until the solution became yellow, ammonia until it gave its odor distinctly to the solution, and then 20 cm.<sup>3</sup> of magnesian sulphate mixture. Portions (75) to (79) inclusive were treated in a similar manner, excepting that 5 cm.<sup>3</sup> of strong hydrochloric acid and no citric acid were added to them. The precipitates of (67), (68), (69) and (70) were filtered off on asbestos, washed, and ignited in the manner previously described. The precipitates of (71), (72), (73) and (74) were filtered off on paper, washed with magnesian sulphate mixture, and then with a few centimeters of ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia, a few centimeters of magnesian sulphate mixture being added after the precipitate had settled. The precipitates of (75) to (79) inclusive were filtered off on paper, washed with magnesian sulphate mixture, dissolved in hydrochloric acid and thrown down again with ammonia, a few centimeters of magnesian sulphate being added after the settling of the precipitate. The second precipitates were filtered off on asbestos, washed and ignited as usual.

	$\text{Mg}_2\text{P}_3\text{O}_7$	$\text{P}_2\text{O}_5$ found.	$\text{P}_2\text{O}_5$ required.	Error.	Per cent. error.
X.	(67) 0.0439 gr.	0.0281 gr.	0.0265 gr.	+ 0.0016 gr.	+ 6.04
	(68) 0.0445 gr.	0.0285 gr.	0.0265 gr.	+ 0.0020 gr.	+ 7.55
	(69) 0.0448 gr.	0.0286 gr.	0.0265 gr.	+ 0.0021 gr.	+ 7.92
	(70) 0.0455 gr.	0.0291 gr.	0.0265 gr.	+ 0.0026 gr.	+ 9.81
	(71) 0.0388 gr.	0.0248 gr.	0.0265 gr.	— 0.0017 gr.	— 6.41
	(72) 0.0390 gr.	0.0249 gr.	0.0265 gr.	— 0.0016 gr.	— 6.04
	(73) 0.0391 gr.	0.0250 gr.	0.0265 gr.	— 0.0015 gr.	— 5.66
	(74) 0.0394 gr.	0.0252 gr.	0.0265 gr.	— 0.0013 gr.	— 4.90
	(75) 0.0421 gr.	0.0269 gr.	0.0265 gr.	+ 0.0004 gr.	+ 1.51
	(76) 0.0426 gr.	0.0272 gr.	0.0265 gr.	+ 0.0007 gr.	+ 2.64

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XIII.	{ (77)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	{ (78)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+ 0.0003 gr.	+ 1.11
	{ (79)	0.0428 gr.	0.0274 gr.	0.0270 gr.	+ 0.0004 gr.	+ 1.48

In experiments (80) to (82) and (85) to (88) inclusive there were added to each portion containing the phosphate and tungstate 0.5 gr. of citric acid, hydrochloric acid until the solution became yellow, ammonia in excess and 20 cm.<sup>3</sup> of magnesian chloride mixture; in experiments (83) and (84), and (89) to (91) inclusive, 5 cm.<sup>3</sup> of strong hydrochloric acid, with no citric acid, ammonia in excess and 20 cm.<sup>3</sup> of magnesian chloride mixture. The precipitates of (85) to (91) inclusive were filtered off on paper, washed with magnesian chloride mixture, dissolved in hydrochloric acid and thrown down again with ammonia. The first precipitates of experiments (80) to (84) and the second precipitates of portions (85) to (91) were collected on asbestos, washed and ignited as usual.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XI.	{ (80)	0.0454 gr.	0.0290 gr.	0.0266 gr.	+ 0.0024 gr.	+ 9.02
	{ (81)	0.0464 gr.	0.0297 gr.	0.0266 gr.	+ 0.0031 gr.	+ 11.65
	{ (82)	0.0466 gr.	0.0298 gr.	0.0266 gr.	+ 0.0032 gr.	+ 12.03
XVI.	{ (83)	0.0444 gr.	0.0284 gr.	0.0269 gr.	+ 0.0015 gr.	+ 5.58
	{ (84)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+ 0.0017 gr.	+ 6.32
XII.	{ (85)	0.0405 gr.	0.0256 gr.	0.0270 gr.	- 0.0014 gr.	- 5.18
	{ (86)	0.0414 gr.	0.0265 gr.	0.0270 gr.	- 0.0005 gr.	- 1.85
	{ (87)	0.0414 gr.	0.0265 gr.	0.0270 gr.	- 0.0005 gr.	- 1.85
	{ (88)	0.0416 gr.	0.0266 gr.	0.0270 gr.	- 0.0004 gr.	- 1.48
XIII.	{ (89)	0.0423 gr.	0.0270 gr.	0.0270 gr.	+ 0.	0.
	{ (90)	0.0424 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	{ (91)	0.0430 gr.	0.0275 gr.	0.0270 gr.	+ 0.0005 gr.	+ 1.85

In experiments (92) to (101) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid were added to each portion containing the phosphate and tungstate, ammonia in distinct excess, magnesian chloride mixture—in (92), (93), (94) and (95) 1.5 cm.<sup>3</sup> and 1.5 cm.<sup>3</sup> more after the precipitate had settled; in (96) and (97) 2 cm.<sup>3</sup>; in (98) and (99) 5 cm.<sup>3</sup>; in (100) and (101) 10 cm.<sup>3</sup> drop by drop, and then 10 cm.<sup>3</sup> more at once—and finally after the precipitate had settled, ammonia until the solution evolved a strong ammoniacal odor.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XIV.	{ (92)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+ 0.0002 gr.	+ 0.74
	{ (93)	0.0427 gr.	0.0273 gr.	0.0269 gr.	+ 0.0004 gr.	+ 1.49
XV.	{ (94)	0.0428 gr.	0.0274 gr.	0.0269 gr.	+ 0.0005 gr.	+ 1.86
	{ (95)	0.0429 gr.	0.0274 gr.	0.0269 gr.	+ 0.0005 gr.	+ 1.86
XIV.	{ (96)	0.0430 gr.	0.0275 gr.	0.0269 gr.	+ 0.0006 gr.	+ 2.23
	{ (97)	0.0431 gr.	0.0276 gr.	0.0269 gr.	+ 0.0007 gr.	+ 2.60
	{ (98)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+ 0.0010 gr.	+ 3.72
	{ (99)	0.0440 gr.	0.0281 gr.	0.0269 gr.	+ 0.0012 gr.	+ 4.46
XV.	{ (100)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+ 0.0013 gr.	+ 4.83
	{ (101)	0.0447 gr.	0.0286 gr.	0.0269 gr.	+ 0.0017 gr.	+ 6.32

In experiments (102) to (115) inclusive 5 cm.<sup>3</sup> of strong hydrochloric acid were added to each portion of phosphate and tungstate, and to portions (112), (113), (114) and (115) 0.5 gr. of citric acid; to every portion, excepting (108) and (109), ammonia in distinct excess; to (108) and (109) ammonia until the precipitate which formed at first was redissolved but not until the solution smelled of ammonia; to all, individually, 20 cm.<sup>3</sup> of magnesian chloride mixture from which the ammonia had been expelled, and, after the settling of the precipitate, ammonia in strong excess.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XV.	{ (102)	0.0436 gr.	0.0279 gr.	0.0269 gr.	+ 0.0010 gr.	+ 3.72
	{ (103)	0.0441 gr.	0.0282 gr.	0.0269 gr.	+ 0.0013 gr.	+ 4.83
XVI.	{ (104)	0.0446 gr.	0.0285 gr.	0.0269 gr.	+ 0.0016 gr.	+ 5.95
	{ (105)	0.0454 gr.	0.0290 gr.	0.0269 gr.	+ 0.0021 gr.	+ 7.80
	{ (106)	0.0459 gr.	0.0294 gr.	0.0269 gr.	+ 0.0025 gr.	+ 9.29
	{ (107)	0.0465 gr.	0.0297 gr.	0.0269 gr.	+ 0.0025 gr.	+ 9.29
XV.	{ (108)	0.0498 gr.	0.0318 gr.	0.0269 gr.	+ 0.0049 gr.	+ 18.21
	{ (109)	0.0543 gr.	0.0347 gr.	0.0269 gr.	+ 0.0078 gr.	+ 28.99
IX.	{ (110)	0.3251 gr.	0.2079 gr.	0.2017 gr.	+ 0.0062 gr.	+ 3.04
	{ (111)	0.3262 gr.	0.2086 gr.	0.2017 gr.	+ 0.0069 gr.	+ 3.39
	{ (112)	0.3381 gr.	0.2178 gr.	0.2017 gr.	+ 0.0161 gr.	+ 7.91
	{ (113)	0.3398 gr.	0.2187 gr.	0.2017 gr.	+ 0.0170 gr.	+ 8.35
	{ (114)	0.3423 gr.	0.2190 gr.	0.2017 gr.	+ 0.0173 gr.	+ 8.49
	{ (115)	0.3429 gr.	0.2193 gr.	0.2017 gr.	+ 0.0176 gr.	+ 8.64

#### *Phosphomolybdates.*

In each of the following experiments upon the determination of phosphoric oxide in phosphomolybdates, 0.5 gr. of molybdic oxide (MO<sub>3</sub>) were dissolved in ammonia and added

to 40 cm.<sup>3</sup> of a phosphate solution, 5 cm.<sup>3</sup> of strong hydrochloric acid added and ammonia in distinct excess. To portions (116) to (120) inclusive were added 20 cm.<sup>3</sup> of magnesian chloride mixture, and to portions (121) to (122) 20 cm.<sup>3</sup> of magnesian sulphate mixture. The first precipitates of (119), (120), (121) and (122) were filtered off on paper, dissolved in hydrochloric acid and thrown down again with ammonia, collected on asbestos (as the first precipitates of the other portions were), washed and ignited as usual. Portions (123) and (124) were precipitated with 1.5 cm.<sup>3</sup> of magnesian chloride mixture, 1.5 cm.<sup>3</sup> being added after the precipitate had settled, together with ammonia in strong excess. Portions (125) to (129) inclusive were precipitated with 20 cm.<sup>3</sup> of magnesian chloride mixture from which the ammonia had been expelled, and ammonia was added in strong excess after the settling of the precipitate.

		Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	P <sub>2</sub> O <sub>5</sub> found.	P <sub>2</sub> O <sub>5</sub> required.	Error.	Per cent. error.
XII.	{ (116)	0.0441 gr.	0.0282 gr.	0.0270 gr.	+ 0.0012 gr.	+ 4.44
	{ (117)	0.0452 gr.	0.0289 gr.	0.0270 gr.	+ 0.0019 gr.	+ 7.04
	{ (118)	0.0458 gr.	0.0293 gr.	0.0270 gr.	+ 0.0023 gr.	+ 8.52
XIII.	{ (119)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	{ (120)	0.0425 gr.	0.0272 gr.	0.0270 gr.	+ 0.0002 gr.	+ 0.74
	{ (121)	0.0423 gr.	0.0271 gr.	0.0270 gr.	+ 0.0001 gr.	+ 0.37
	{ (122)	0.0427 gr.	0.0273 gr.	0.0270 gr.	+ 0.0003 gr.	+ 1.11
XVI.	{ (123)	0.0423 gr.	0.0270 gr.	0.0269 gr.	+ 0.0001 gr.	+ 0.37
	{ (124)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+ 0.0002 gr.	+ 0.74
	{ (125)	0.0424 gr.	0.0271 gr.	0.0269 gr.	+ 0.0002 gr.	+ 0.74
	{ (126)	0.0425 gr.	0.0272 gr.	0.0269 gr.	+ 0.0003 gr.	+ 1.11
IX.	{ (127)	0.3168 gr.	0.2026 gr.	0.2017 gr.	+ 0.0009 gr.	+ 0.44
	{ (128)	0.3173 gr.	0.2030 gr.	0.2017 gr.	+ 0.0013 gr.	+ 0.64
	{ (129)	0.3180 gr.	0.2033 gr.	0.2015 gr.	+ 0.0016 gr.	+ 0.79

Experiments (1) to (10) inclusive (11), (13) and (15) demonstrate that the method of estimating the phosphoric oxide of alkaline phosphates by precipitation with magnesian sulphate mixture and washing until the chlorine reaction vanishes from the filtrate gives results far too high when the amount of the precipitant used is in any considerable excess of the amount theoretically required. Thus, in experiments (1) to (6), in each of which 20 cm.<sup>3</sup> of magnesian sulphate mixture were used, the amount required by theory being about 5.2 cm.<sup>3</sup>, the

error varies from  $+ 0.0033$  gr. to  $+ 0.0060$  gr. on  $0.1298$  gr. of phosphoric oxide, or from  $+ 2.54$  to  $+ 3.39$  per cent.; in experiments (7) to (10), in each of which  $20\text{ cm.}^3$  of the precipitant were used, while theory requires about  $1.1\text{ cm.}^3$ , the error upon  $0.0265$  gr. of phosphoric oxide varies from  $+ 0.0004$  gr. to  $+ 0.0021$  gr., or from  $+ 1.51$  to  $+ 7.92$  per cent.; in experiment (11) in which  $6\text{ cm.}^3$  of the precipitant were used, while about  $2.1\text{ cm.}^3$  were theoretically required, the error is  $+ 0.0007$  gr. upon  $0.0512$  gr. of phosphoric oxide, or  $+ 1.37$  per cent.; and in experiments (13) and (15), in which  $12\text{ cm.}^3$  of the precipitant were used, while about  $2.1\text{ cm.}^3$  were theoretically required, the error upon  $0.0512$  gr. of phosphoric oxide was  $+ 0.0017$  gr., or  $+ 3.31$  per cent.

Experiments (21) to (26) inclusive show that when the process was varied so as to precipitate the phosphate solution, either containing no free ammonia or a very small quantity, by a magnesian sulphate mixture from which the ammonia had been expelled, the error of the result varied from  $+ 0.0061$  gr. to  $+ 0.0117$  gr. upon  $0.1875$  gr. of phosphoric oxide, or from  $+ 3.25$  to  $+ 6.24$  per cent.; and from  $+ 0.0077$  gr. to  $+ 0.0106$  gr. upon  $0.2142$  gr. of phosphoric oxide, or from  $+ 3.59$  to  $+ 4.94$  per cent.—the greatest errors appearing naturally in the experiments made with hot solutions containing no free ammonia in which cases the hydro-magnesian phosphate first thrown down was partially changed into tri-magnesian phosphate by the action of the heat, and therefore not converted into ammonio-magnesian phosphate upon the subsequent addition of ammonia.

Experiments (12), (14), (16) and (17) to (20) inclusive indicate that tolerably good results may be obtained by draining the first precipitate, dissolving in hydrochloric acid and reprecipitating with ammonia; the first three experiments showing incidentally that the addition of small amounts of citric acid does not prevent precipitation to any very marked degree in presence of a considerable excess—in this case about  $10\text{ cm.}^3$  to  $0.5$  gr. of citric acid—of magnesian sulphate mixture. Thus in experiments (12), (14) and (16) the error was  $0$ ; and in experiments (17) to (20) the error varied from  $+ 0.0006$  gr. to  $+ 0.0015$  gr. on  $0.1863$  gr. of phosphoric oxide, or from  $+ 0.32$  to  $+ 0.80$  per cent., the mean error being about  $+ 0.0006$  gr., or  $+ 0.32$  per cent.

It appears from these experiments that the method of precipitating by magnesic sulphate mixture without the solution and second precipitation ought to give an accurate determination of phosphoric acid, providing only that the amount of the precipitant used were just sufficient to complete the precipitation. But this condition renders the process practically useless in ordinary cases; and inasmuch as in Kissel's method of compensating for enclosed material by excessive washing, the amount of washing must necessarily be proportioned both to the weight of phosphoric acid present and to the excess of the precipitant,—elements which introduce a great deal of uncertainty,—it would appear that if magnesic sulphate mixture is to be the precipitant the method of precipitating twice is the only one which can be relied upon on all occasions to give tolerably correct results.

The results obtained in experiments (27) to (66) by precipitating with magnesic chloride mixture are different as the method of treatment varies. It will be noticed that in experiments otherwise essentially similar the variations in the amount of the precipitant produce differences in the results. Thus, in experiments (27) to (43), in which 10 cm.<sup>3</sup> or 12 cm.<sup>3</sup> of the precipitant were used, the error varies from — 0.0008 gr. to + 0.0012 gr., or from — 0.42 to + 0.64 per cent., the mean error being nearly 0; while in the experiments (48) to (53), in which 40 cm.<sup>3</sup> of the precipitant were used, the error varies from + 0.0011 gr. to + 0.0016 gr., or from + 0.60 to + 0.87 per cent., the mean error being about + 0.0013 gr., or + 0.71 per cent. It will be seen also that while it makes no apparent difference whether the precipitant is added to the phosphate directly, as in (27) and (28), or after treatment with hydrochloric acid, as in (29) to (39), the dissolving of a precipitate, by adding hydrochloric acid to the supernatant liquid, and reprecipitation with ammonia tend to reduce the results below those of experiments in which this has not been done, but which are similar in other respects. This appears very distinctly in a comparison of experiments (40) and (41) with (42) and (43), where the mean error is reduced from about + 0.0010 gr. upon 0.1875 gr. of phosphoric oxide, or from + 0.56 per cent. to 0; or of experiments (44) and (45) with (46) and (47), where the mean error is reduced from

+ 0.0022 gr. to about + 0.0003 gr. upon 0.1885 gr. of phosphoric oxide, or from + 1.17 to + 0.18 per cent.

It appears, further, from a comparison of experiments (54) to (58) with experiments (48) to (53), that results got by precipitating solutions containing either no free ammonia, as in (56), (57) and (58), or only a small amount, as in (54) and (55), by a magnesian chloride mixture deprived of ammonia are more nearly correct than those got by precipitating under essentially similar conditions with the ammoniacal magnesian chloride mixture, as in (48) to (53). Thus, in (48) to (53) the error varies from + 0.0011 gr. to + 0.0016 gr. upon 0.1831 gr. of phosphoric oxide, or from + 0.60 to + 0.87 per cent., the mean error being about + 0.0013 gr. or + 0.71 per cent.; while in (54) to (58) the error varies from 0 to + 0.0012 gr. upon 0.1831 gr. or 0.1875 gr. of phosphoric oxide, or from 0 to 0.64 per cent., the mean error being about + 0.0004 gr. or + 0.22 per cent.; and it is to be remarked that in (54), (55) and (56), in which dilute ammonia was added after the non-ammoniacal magnesian chloride mixture, the mean error—about + 0.0002 gr. or + 0.10 per cent.—is much smaller than the mean error of (57) and (58)—about + 0.0008 gr., or + 0.44 per cent.—in which strong ammonia was added after the non-ammoniacal magnesian chloride mixture. The high results of experiments (59) and (60), in which the non-ammoniacal magnesian chloride mixture was added to the hot phosphate solution, are explained by the fact that a part of the hydromagnesian phosphate first formed was decomposed by the heat with the formation of trimagnesian phosphate, and therefore not completely converted into ammonio-magnesian phosphate by the ammonia subsequently added. From experiments (61) to (64) it will be seen that the presence of 3 gr. of sodic chloride in the phosphate solution raises the figures of the analysis materially when precipitation is effected by the ammoniacal magnesian chloride mixture, even with small weights of phosphoric oxide, and that better results are got in (65) and (66) by using the non-ammoniacal mixture.

The use of an excessive quantity, too, of ammoniac chloride tends apparently to reduce the error. Thus, in experiments (48) to (53) the mean error was about + 0.0013 gr., or + 0.71 per cent., while in (44) and (45), in which free ammonia, but

no ammoniac chloride beyond the amount in the magnesian chloride mixture, was used, the mean error is  $+ 0.0022$  or  $+ 1.17$  per cent., although less of the precipitant was used in the latter.

The cause of all these differences in the accuracy of the determination of the phosphoric oxide of alkaline phosphates by precipitation with magnesian chloride mixture seems to lie in the variations of the rapidity with which the ammonio-magnesian phosphate is crystallized from solution. The sudden addition of a large amount of the precipitant, or of an excess of the precipitant to a strongly ammoniacal solution of the phosphate, or of strong ammonia to a solution of the precipitate in acid, tends to hasten the deposition, and so to prevent the complete exclusion of foreign material from the crystalline structure; while in the precipitation of solutions containing large amounts of ammoniac chloride, or of weakly ammoniacal solutions, or of solutions of the precipitate in acid, by the gradual addition of ammonia the process of crystallization goes on more slowly and perfectly.

The differences between results got by using a magnesian sulphate mixture and those obtained with a magnesian chloride mixture may be, perhaps, partly explained by the supposition that magnesian sulphate resists exclusion during the crystallization of the ammonia-magnesian phosphate more effectively than magnesian chloride, and partly by the fact that magnesian sulphate enclosed in a precipitate would probably not change materially in composition during an ignition over a Bunsen burner in a crucible standing on platinum foil, while magnesian chloride ignited in presence of aqueous vapor under like circumstances would be converted into magnesian oxide whose molecular weight is but one-third of that of the sulphate. It is difficult, at all events, to conceive how the contamination of the precipitate can be other than mechanical; for the trimagnesian phosphate could only be produced by a reaction between the ammonio-magnesian phosphate and magnesian sulphate,—which is quite improbable, at least in the cold,—and the formation of a magnesian hydrate or basic sulphate would seem to be altogether unlikely under the circumstances.

In the experiments upon the phosphotungstates the mean error of the method involving a single precipitation with magnesian sulphate mixture (experiments 67 to 70) was about  $+0.0021$  gr. upon  $0.0265$  gr. and with magnesian chloride mixture (experiments 80 to 84) about  $+0.0024$  gr., upon  $0.0266$  gr. or  $0.0269$  gr., of phosphoric oxide, or about  $+8.44$  per cent. The mean error of the method of double precipitation upon nearly the same amounts of phosphoric oxide, the precipitant alone being used to wash the first precipitate and no citrate being present, was, with magnesian sulphate mixture (experiments 75 to 79) about  $+0.0004$  gr., or  $+1.51$  per cent., and with magnesian chloride mixture (experiments 89 to 91)  $+0.0002$  gr., or  $+0.74$  per cent.; the mean error when the first precipitate by magnesian sulphate mixture was washed with the precipitant and afterwards with ammonia water (experiments 71 to 74) being about  $-0.0015$  gr., or  $-5.66$  per cent.; and when the first precipitate was thrown down in presence of a citrate by magnesian chloride mixture and washed with the precipitant (experiments 85 to 88), about  $-0.0007$  gr., or  $-2.59$  per cent. When precipitation was effected with  $1.5$  cm.<sup>3</sup> of magnesian chloride mixture, the same being added after precipitation (experiments 92 to 95) the mean error upon  $0.0269$  gr. of phosphoric oxide was  $+0.0004$  gr. or  $+1.49$  per cent.; when by  $2$  cm.<sup>3</sup> (experiments 96 and 97) about  $+0.0006$  gr., or  $+2.23$  per cent.; when by  $5$  cm.<sup>3</sup> (experiments 98 and 99)  $+0.0011$  gr., or  $+4.09$  per cent.; and when by  $10$  cm.<sup>3</sup> added drop by drop, with  $10$  cm.<sup>3</sup> more subsequent to precipitation (experiments 100 and 101)  $+0.0015$  gr., or  $+5.58$  per cent. The mean error of the determination by precipitating with  $20$  cm.<sup>3</sup> of non-ammoniacal magnesian chloride mixture, in slightly ammoniacal solutions (experiments 102 to 107 and 110 to 115) was about  $+0.0018$  gr. upon  $0.0269$  gr. of phosphoric oxide, or  $+6.69$  per cent.; about  $+0.0065$  gr. upon  $0.2017$  gr. of phosphoric oxide, or  $+3.22$  per cent., in solutions containing no citrate, and in solutions containing a citrate  $+0.0170$  gr., or  $+8.35$  per cent. The mean error when  $20$  cm.<sup>3</sup> of non-ammoniacal magnesian chloride mixture was added to the solution of phosphate and tungstate containing no free ammonia (experiments 108 and 109) amounted to about  $+0.0063$  gr. upon  $0.0269$  gr. of phosphoric oxide, or  $+23.60$  per cent.

The use of citric acid in many of the experiments above, in accordance with a suggestion of Dr. Gibbs, appears to be attended with unfavorable results. Thus in experiments (85) to (88), in which the first precipitates were dissolved and reprecipitated, this appears to have lowered the results below those of (89) to (91); while in experiments (80) to (82) and in experiments (112) to (115), in which the first precipitate was not dissolved, it appears to have raised the results above those of (83) and (84), and (110) and (111) respectively,—facts which are perhaps to be explained by attributing to the citrate both a solvent and contaminating action upon the precipitate.

Of the experiments upon the phosphomolybdates (123) and (124), in which the precipitation was effected by 1.5 cm.<sup>3</sup> of magnesian chloride mixture, 1.5 cm.<sup>3</sup> of the same being added afterward, show a mean error of less than + 0.0002 gr. upon 0.0269 gr. of phosphoric oxide, or + 0.55 per cent.; and experiments (116) to (118) in which 20 cm.<sup>3</sup> of the same precipitant were employed + 0.0018 gr. upon 0.0270 gr. of phosphoric oxide, or + 6.66 per cent.; experiments (119) to (122), in two of which the precipitation was effected by magnesian sulphate mixture, and in two by magnesian chloride mixture, the first precipitate being washed with the precipitant, dissolved in hydrochloric acid and again thrown down, less than + 0.0002 gr. upon 0.0270 gr. of phosphoric oxide, or + 0.65 per cent. In experiments (125) to (129) in which 20 cm.<sup>3</sup> of the magnesian chloride mixture deprived of ammonia were added to slightly ammoniacal solutions, the mean error was less than + 0.0003 gr. on 0.0269 gr. of phosphoric oxide, or + 0.92 per cent., and less than + 0.0013 gr. on 0.2017 gr. of phosphoric oxide, or + 0.62 per cent.

It will be noticed that in the experiments with phosphates and phosphomolybdates a large excess of the magnesian chloride mixture was not markedly prejudicial to the accuracy of results when precautions were taken to induce a slow formation of the precipitate, while in the experiments with phosphotungstates the reverse was true. The reason for this exceptionally unfavorable action in the case of the phosphotungstates is probably indicated in the facts that the addition of free ammonia beyond a certain amount to the solution of a

phosphotungstate produces turbidity, and that the addition of magnesia mixture to a clear solution of normal sodic tungstate, ammonic chloride and ammonia renders the solution opalescent and occasions the deposition, after some hours, of an almost invisible precipitate; but it is to be noted in this connection that the action of magnesia mixture upon a clear ammoniacal solution of ammonic molybdate and ammonic chloride is similar to its action upon the tungstate solution.

*Summary.*

It would appear from the preceding account that in determining the phosphoric oxide of alkaline phosphates, free from sulphates or other substances likely to contaminate a precipitate, accuracy is most conveniently and surely attained by adding to the somewhat dilute solution of the phosphate ammonia in slight but quite distinct excess, then an excess of magnesian chloride mixture containing no free ammonia (made by dissolving three parts of crystallized magnesian chloride and eight parts of ammonic chloride in water, adding water containing ammonia until the volume of the solution reaches forty-eight parts, filtering and boiling off the free ammonia), and, after the precipitate has settled, ammonia until the liquid evolves a strong odor of it. In determining the phosphoric oxide of phosphotungstates the best results are to be got by adding to the solution containing free ammonia an excess of either of the magnesia mixtures, washing the precipitate with the precipitant, dissolving in hydrochloric acid, diluting if necessary and reprecipitating with a little dilute ammonia, adding strong ammonia after the precipitate has settled; or, when working with small amounts, by proceeding as in the case of the phosphates, taking special care, however, that the solution is distinctly ammoniacal before precipitating, and that no great excess of the precipitant is used. In the determination of the phosphoric oxide of phosphomolybdates, the method recommended for use in the case of the phosphates serves very well when the amount of phosphoric oxide does not exceed (let us say) 0.05 gr., but for amounts larger than this the method of double precipitation recommended for the phosphotungstates is more accurate.

As to the time which should be allowed to pass between

precipitating and filtering, my experiments support those of Abesser, Jani, and Maereker\* in pointing to the condition that a precipitate may be filtered with safety as soon as it has completely subsided, or, after ten or fifteen minutes.

The use, for the filtration and ignition of the precipitate, of the method which I have employed in the experiments described above greatly expedites the analysis. Thus, with two perforated crucibles at my disposal, I have completed within four and one-half hours from the measuring out of the first solution seven determinations of the phosphoric oxide of an alkaline phosphate,—the ignition of each precipitate requiring less than five minutes.

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## LABORATORY NOTES.

BY ARTHUR MICHAEL.

### I.—ON MONO-ETHYLPHTHALATE.

The aim of the following experiments, made several years ago, was the preparation of ortho-formylbenzoic acid, and for which purpose mono-ethylphthalate was subjected to the action of phosphorus trichloride, in the hope of obtaining the chloride of that compound, which I intended to reduce with nascent hydrogen.

To prepare mono-ethylphthalate absolute alcohol was allowed to act on phthalic anhydride, a reaction similar to that of the formation of mono-ethylsuccinate by the action of alcohol on succinic anhydride.† Equal parts of absolute alcohol and phthalic anhydride were heated in a flask connected with an upright condenser for ten hours at 100°. The whole of the anhydride was never converted into the ether in question, even if the time of heating was prolonged and the relative amount of alcohol to anhydride greatly increased. The excess of alcohol was evaporated at a low

\* *Zeitschrift f. anal. Chem.* XII. 250.

† Heintz, *Pogg. Ann.* 108, 70.

temperature, and the residue which remained was dissolved in water and neutralized in the cold with pure barium carbonate, thus forming the barium salts of mono-ethylphthalate and phthalic acid. To effect a separation of the two salts advantage was taken of their different solubility in water; the former salt being extremely soluble in moderately warm water, whereas barium phthalate is much less soluble. The precipitate which settled on neutralization was therefore barium phthalate, and by evaporating the filtrate from this precipitate to a small bulk, and filtering the solution while warm from the precipitate which had then settled, and, if necessary, repeating the operation again, the two barium salts were easily separated. The filtrate yielded on cooling the barium salt of the new acid in long, concentrically grouped, white needles, which are very soluble in cold and in all proportions in warm water.

The barium analyses showed that this salt has the formula  $(\text{C}_6\text{H}_4\text{COOC}_2\text{H}_5)_2\text{Ba}$ .

.5360 gr. of substance, dried at  $100^\circ$ , gave .2405 gr. of barium sulphate.

.6812 gr. gave .3148 gr. of barium sulphate.

		Calculated.	Found.	
			I.	II.
Ba.	...	27.24	26.83	27.17

A concentrated aqueous solution of the barium salt is precipitated by silver nitrate, forming the corresponding silver salt. This salt crystallizes from water in beautiful, long needles, which on exposure to the light soon blacken. They are moderately soluble in cold and quite soluble in warm water.

The results of the silver analyses correspond with the formula  $\text{C}_6\text{H}_4\begin{matrix} \diagup \text{COOC}_2\text{H}_5 \\ \diagdown \text{COOAg} \end{matrix}$ .

.5210 gr. of substance, dried in vacuo, gave, after ignition, .1883 gr. of metallic silver.

.6364 gr. gave .2314 gr. of silver.

.5776 gr. gave .2078 gr. of silver.

		Calculated.	Found.		
			I.	II.	III.
Ag	...	35.88	36.11	36.33	35.98

The free mono-ethylphthalate was easily obtained by treating an aqueous solution of the barium salt with the calculated amount of sulphuric acid, and evaporating the filtrate from the barium sulphate in *vacuo*, and is a heavy oil which is moderately soluble in water. It is remarkably unstable towards heat; upon distillation it decomposes in phthalic anhydride and alcohol, and gradually undergoes the same decomposition when heated upon a water-bath.

To obtain the chloride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{COOC}_2\text{H}_5 \\ \diagdown \text{COCl} \end{smallmatrix}$ , equivalent quantities of mono-ethylphthalate and phosphorus trichloride were mixed in a retort connected with a condenser, and, finding that no reaction ensued in the cold, the retort was gently warmed on a water-bath. The reaction was quite violent, and a considerable quantity of chlorhydric acid was evolved. The contents of the retort were then treated with cold water, and left a heavy oil, which was dried over  $\text{H}_2\text{SO}_4$  in *vacuo*.

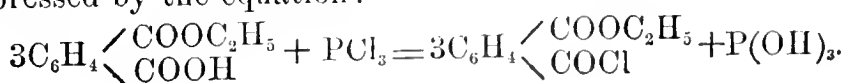
The oil was found to be free from chlorine. A proximate analysis gave results which correspond with the formula of di-ethylphthalate, and a comparison of the properties and boiling points of the two substances showed them to be identical.

.2218 gr. of substance gave .5284 gr. of  $\text{CO}_2$  and .1301 gr. of  $\text{H}_2\text{O}$ .

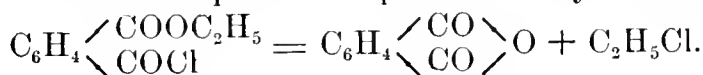
	Calculated for $\text{C}_6\text{H}_4(\text{COOC}_2\text{H}_5)_2$	Found.
C	... 64.86	64.97
H	... 6.30	6.52

The reaction, evidently, proceeded quite differently from that anticipated, and I deemed it advisable to examine the gases formed in the reaction more thoroughly. On passing the gases evolved through water only a portion was absorbed, which proved to be chlorhydric acid; the unabsorbed portion burned with a green flame and contained chlorine. On passing through a tube placed in a cooling mixture it condensed to a volatile liquid, which proved to be ethylchloride.

The first step in the above described reaction is doubtless the formation of  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{COOC}_2\text{H}_5 \\ \diagdown \text{COCl} \end{smallmatrix}$ , a reaction which may be expressed by the equation:



But the chloride of mono-ethylphthalate possesses that remarkable property of the phthalic compounds of undergoing easily a condensation, and even at the temperature of the reaction it decomposes into phthalic anhydride and ethylchloride:



To explain the formation of di-ethylphthalate, we may suppose that part of the ethylchloride acted on unchanged mono-ethylphthalate, forming chlorhydric acid and di-ethylphthalate.

The action of phosphorus pentachloride on mono-ethylphthalate proceeded in the cold, and I hoped to obtain the chloride in this way; but I found the reaction was in this case similar to that of the trichloride, the same products being formed.

The described reaction illustrates well the condensation power of the phthalic compounds, since the analogous compounds  $\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \text{COCl} \end{array}$  and  $\text{C}_2\text{H}_4 \begin{array}{c} \diagup \text{COOC}_2\text{H}_5 \\ \diagdown \text{COOH} \end{array}$  can both be distilled without undergoing decomposition.

## II.—ON A NEW FORMATION OF ETHYL-MUSTARD OIL.

A. W. Hofmann,\* shortly after Gautier and himself demonstrated that the alkylcarbamines could be obtained by the action of alkyl iodides on silver cyanide, examined the action of ethyl iodide on silver sulphocyanate, in the hope of obtaining ethyl-mustard oil. He found, however, that only ethyl-sulphocyanate was formed in the reaction. Several years later, V. Meyer,† after the remarkable results obtained from silver nitrite, repeated this experiment, and obtained as result the sulphocyanate free from even the slightest trace of mustard oil. These results evidently indicate, that the silver atom in silver sulphocyanate is joined with the sulphur and not with the nitrogen atom, a molecular juxtaposition which is doubtless owing to the greater affinity of silver for sulphur than for nitrogen.

It seemed possible by employing a metallic sulphocyanate, in which the metal had a greater affinity for nitrogen and a

\* Monatsber. d. ber. Acad. 1867, 650.

† Ann. Chem. 171, 47.

less affinity for sulphur than silver, that mustard oils might be obtained by the action of alkyl iodides on such a salt. I was therefore induced to reinvestigate the action of ethyl iodide on mercuric sulphocyanate. Schlagdenhauffen\* had already made this experiment; he obtained ethylsulphocyanate and a red mass, which was not further examined.

Ethyl iodide acts on mercuric sulphocyanate even at  $100^{\circ}$ , but I found it advisable to heat the mixture at a higher temperature. For this purpose a tube containing 20 gr. of  $\text{Hg}(\text{SCN})_2$  and 30 gr. of  $\text{C}_2\text{H}_5\text{I}$  was heated for about two and one-half hours at  $140\text{--}150^{\circ}$ . Upon opening the tube the strong penetrating odor of ethyl-mustard oil was observed, and a dark red sediment had formed. The contents of the tube were brought into a flask connected with a condenser, and treated with steam as long as an oil passed over. This oil was separated from the supernatant water, dried over calcium chloride and distilled; that portion which passed over under  $135^{\circ}$  was collected separately. The penetrating odor of this portion indicated the presence of ethyl-mustard oil in it, but the small quantity of oil obtained, although I had used a number of the tubes, only allowed a very imperfect separation from the sulphocyanate, which is formed in much greater quantity in the reaction than its isomer. To prove the presence of ethyl-mustard oil in the lower boiling portion it was mixed with aniline, and the mixture allowed to stand for several days. A crystalline precipitate gradually settled from the liquid, which also lost the odor of mustard oil and had now that of ethyl-sulphocyanate. The precipitate was purified by crystallization from water, and a comparison of its properties with those of phenyl-ethyl-sulphocarbamide† showed that the two compounds were identical, thus proving indirectly the presence of ethyl-mustard oil in the original liquid. The amount of mustard oil formed in this reaction is very small—I should judge about three per cent. of the amount of sulphocyanate; but even this compound is formed in quantities which are very small in comparison to the amount of the ingredients employed. The red mass mentioned by Schlagdenhauffen is the principal product of the reaction. This red compound is possibly a

\*Ann. ch. phys. (3), 56, 297.

† Weith—Deutsch. ch. Gesell. Ber 1875, 1524.

double compound of ethyl-mustard oil with mercuric iodide; it contains Hg, C, S and I. It yields upon distillation a heavy oil containing sulphur. I hoped to decompose it by boiling with a concentrated aqueous solution of potassium cyanide, as Gautier decomposed the compound  $C_2H_5NCAgNC$ , but it proved to be without action on it.

Methyl and amyl iodides acted in a similar manner on mercuric sulphocyanate, and formed liquids which had the strong penetrating odor of mustard oils. Although the method is of no importance for the preparation of mustard oils, still it is of theoretical interest as characterizing an important difference in the action of paraffin iodides on the mercuric and silver salts of sulphocyanic acid.

### III.—ON THE PREPARATION OF METHYL ALDEHYDE.

I have lately had occasion to use a considerable quantity of methyl aldehyde, and found that the methods hitherto in use only permitted its preparation in large amounts with much difficulty. This is the case with the method of Butlerow\* and that of Heintz.† The method recently proposed by A. W. Hofmann,‡ by the oxidation of methyl alcohol, yields a dilute methylalcoholic solution of the aldehyde, but this solution is much less adapted to my purpose than an aqueous solution. I have found that the action of water on mono-chlormethylacetate, a compound discovered by L. Henry § by the action of chlorine on methylacetate, yields almost the theoretical amount of an aqueous solution of methyl aldehyde.

For the preparation of mono-chlormethylacetate 500 gr. of methylacetate were placed in a flask surrounded by cold water and connected with a condenser, and a current of dry chlorine gas passed through the liquid in the flask for about seven hours. The contents of the flask were distilled, and that portion distilling between  $90-130^\circ$  was finally redistilled; the portion which now passed over between  $100-120^\circ$  was mono-

\* Ann. Chem. Pharm. 144, 38.

† Ann. Chem. Pharm. 138, 40.

‡ Ber. d. chem. Gesell. 1878, 1685.—The formation of methylaldehyde by the oxidation of methylalcohol may easily be shown in the lecture-room by allowing a drop of methylalcohol to fall on a heated platinum crucible so that it takes a spheroidal state; the strong penetrating odor of the aldehyde is almost immediately noticed.

§ Ber. d. chem. Gesell. 1873, 42.

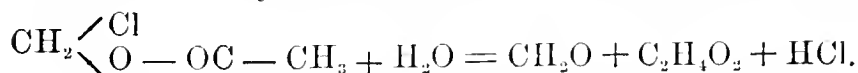
chlormethylacetate. The portion boiling under  $100^{\circ}$  may be again subjected to the action of chlorine, and yields a further quantity of mono-chlormethylacetate. The yield of the mono-chlor-compound is very satisfactory, and it may be obtained in this manner in large quantities.

Henry, in the above-mentioned memoir, has already called attention to the fact that this compound is easily decomposed by alkalis, and gives rise to the odor of methyl aldehyde. It is, however, preferable to decompose it with water. For this purpose 110 gr. of mono-chlormethylacetate and 55 gr. of distilled water were heated in a strong, closed flask for about one-half to one hour\* at  $100^{\circ}$ . The water, which at first formed a layer over the ether, mixed, after being heated for that time, to form a homogeneous liquid, which smelt strongly of methyl aldehyde. The contents of the flask were neutralized exactly with a very concentrated solution of sodium hydrate, about 73 gr. of that compound being necessary to neutralize the amount taken. The solution thus obtained was distilled from a flask placed in an oil-bath, and yielded a colorless distillate, which was usually slightly acid, and which was easily obtained neutral by a subsequent neutralization and distillation. The white solid remaining in the flask consisted of sodium chloride and acetate. From 110 gr. of chlor-methylacetate about 140–150 gr. of the aqueous solution were obtained, and which contained 16 to 18 per cent. of methyl aldehyde, as the following estimations show:

13 gr. of solution treated with  $\text{H}_2\text{S}$  yielded 2.34 gr. of thioformaldehyde.

20 gr. yielded 3.28 gr. of thioaldehyde.

The formation of methylaldehyde by the action of water on mono-chlormethylacetate may be expressed by the equation:



10 gr. of mono-chlorether should yield, according to this equation, 2.76 gr. of  $\text{CH}_2\text{O}$ , and 2.34 gr. were obtained, that is, 81 per cent. of the theoretical yield.

Trioxymethylene may be obtained from the solution in question by allowing it to evaporate in vacuo, but not without considerable loss; 26 gr. of solution yielded 2.17 gr. of

\* If heated too long the flask opened under strong pressure.

trioxymethylene, which is about 40 per cent. of the theoretical yield. The aqueous solution of methyl aldehyde evaporates in vacuo to about one-third of its original bulk before a separation of trioxymethylene begins, and in this manner an aqueous solution containing about 40 per cent. of methyl aldehyde may be obtained.

This method has allowed me to obtain a large quantity of methyl aldehyde, and to examine its behavior towards potassium and sodium salts, as well as the alkaline bases. I have obtained very interesting results, which I shall describe later.

#### IV.—ON THE “MIGRATION OF ATOMS IN THE MOLECULE” AND REIMER'S CHLOROFORM ALDEHYDE REACTION.

The formation of a liquid in the action of aniline chlorhydrate on methyl alcohol at a high temperature, which boiled at a higher temperature than dimethylaniline, was first observed by Chas. Lauth,\* and he considered the liquid thus formed as consisting of polymers of that compound. Several years later A. W. Hofmann and C. A. Martius† examined this oil more thoroughly, and succeeded in isolating from it dimethyltoluidine, and even higher homologues of dimethylaniline. Hofmann and Martius explained the formation of these compounds in that the methyl chloride formed in the reaction, after having substituted the hydrogen atoms of the amido-group, attacked the hydrogen of the benzene nucleus. Later, Hofmann,‡ in a remarkable memoir, again returned to this subject, and by a series of interesting experiments threw new light on the nature of this reaction. He stated that naturally the formation of tri-methylphenylammonium chloride would, in the first place, be expected, and was therefore induced to examine the behavior of the corresponding iodide under similar conditions towards heat. This compound yielded, when heated at 230°C. in a closed tube, a mixture of two isomeric toluidines and methylxylylidine; at the temperature of melting lead, cumidine. The explanation given by Hofmann of these facts is the “migration of atoms in the molecule,” the methylgroups changing places with the hydrogen atoms of the benzene nucleus.

\* Bull. soc. chim. [2] 7, 448.

† Ber. d. chem. Gesell. 1871, 742.

‡ Ber. d. chem. Gesell. 1872, 704.

It seemed to me that by considering the behavior of the tetra-alkylammonium halogens on distillation a more intimate knowledge of the nature of the reaction in question might be obtained. These compounds decompose at a high temperature into tri-alkylamines and alkylhalogens. Bearing on this subject is also the behavior of the haloid acid salts of di- and tri-alkylamines towards heat, and which decompose into mono- and di-alkylamines and alkylhalogens.

Let us now consider the behavior of tri-methylphenylammonium iodide when heated in a closed tube at a high temperature. The first result would be its decomposition into di-methylaniline and methyl iodide; and when we consider the facility with which benzoylchloride, chloroform, phosphorus tri-chloride and other halogen compounds act on the hydrogen of the benzene nucleus in di-methylaniline, there is little doubt that under the favorable conditions of a high temperature, and where the direct combination is impossible, the methyl iodide would act on the hydrogen of the benzene nucleus, forming di-methyltoluidine and iodhydric acid. The acid thus formed then acts on the di-methyltoluidine,\* forming mono-methyltoluidine and methyl iodide. The latter compound acts on the hydrogen of the nucleus forming mono-methylxyldine and methyl iodide; and these compounds again reacting in a like manner, give as final products iodhydric acid and cumidine. That a higher temperature is necessary to realize the two last steps of the reaction, is owing to the stability of the dimethyltoluidine towards iodhydric acid at a temperature at which tri-methylphenylammonium iodide already decomposes into dimethylaniline and methyl iodide.

By the action of aniline chlorhydrate on an excess of methyl alcohol Hofmann and Martius obtained, as already mentioned, homologues of dimethylaniline. This result is due to the facility with which chlorhydric acid acts on methyl alcohol, and it is easy to understand that, in this case, aniline chlorhydrate would be finally converted in penta-methyl-dimethylaniline chlorhydrate, providing sufficient methyl alcohol were present, and the time of heating sufficiently prolonged. Hofmann † also examined the behavior of the chlor-

\* Methyltoluidine distilled in a current of chlorhydric acid yields toluidine and methylchloride.—Lauth (Bull. soc. chim. [2] 19, 489).

† Deutsch. ch. Ges. Ber. 1872, 720.

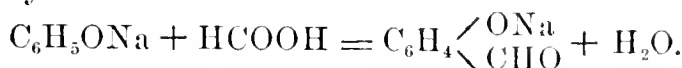
and iodhydrates of mono-methylaniline in a closed tube at  $350^{\circ}$ , and found that the former salt yielded para-toluidine, while from the latter salt the ortho-compound was obtained. That methyl chloride and iodide should form isomers in their action on the hydrogen of the benzene nucleus would not be in the least unexpected; but I believe a clue to the different results obtained in these *reactions* will be found in the greater stability of methylaniline chlorhydrate towards heat, than the iodhydrate of the base. It is hardly necessary to mention instances in which when both ortho- and para-substitution products of benzene are simultaneously formed, where the relative amount of each of the isomers formed depends on the temperature at which the reaction proceeded; the ortho-derivative predominating when a moderate, and the para-compound when a high temperature is employed. If then the iodhydrate decomposes into aniline and methyl iodide at a temperature lower than the chlorhydrate does into aniline and methyl chloride, it would naturally tend to form an ortho-derivative. Moreover, it is very probable that methyl iodide is able to substitute the hydrogen of the nucleus at a lower temperature than methyl chloride, and this property doubtless plays a role in the different results obtained.

The above considerations make it probable that were the vapors of methyl chloride and aniline, both heated to a temperature above that at which methylaniline chlorhydrate decomposes into methyl chloride and aniline, and the gases mixed at this temperature, para-toluidine would in this manner be formed.

A reaction apparently of an altogether different nature from that we have just considered, is the formation of ortho- and para-oxybenzoic aldehydes by the action of an aqueous solution of sodium hydrate and chloroform on phenol, which was discovered by K. Reimer\* in 1876. Reimer and Tiemann,† in a subsequent paper, called attention to the analogy of the reaction in question to that of the formation of salicylic acid, by the action of carbonic acid on sodium *phenolate*, since the formic acid containing an atom less of oxygen than carbonic acid, would, therefore, form the aldehyde corresponding to the acid obtained by the action of carbonic acid. H. Kolbe‡

\* Ber. d. chem. Gesell. 1876, 423.    † Ibid. 1876, 826.    ‡ J. p. Chem. (N. F.), 14, 332.

lays stress on the fact that the formic acid which enters into this reaction is in a nascent state; the reaction expressed graphically is:



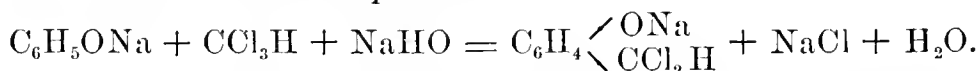
But can we well suppose that formic acid formed in the presence of a strong alkali would not immediately enter into chemical combination with it, to form a formate? It was, however, a question of experiment whether formic acid would act on a mixture of sodium hydrate and phenol to form aromatic oxy-aldehydes, and all experiments in this direction have given negative results. Evidently, if formic acid is the means of introducing the formyl group in phenol, it must have properties which are quite different from those of the acid commonly understood under this name, and, in fact, both Kolbe, and Reimer and Tiemann, attach importance to the fact that the acid entering into this reaction is in a nascent state. But, we may ask, how explain the different properties of nascent and free formic acid? Is it not the same acid, and in the same molecular state?

The comparison between the action of carbonic acid and chloroform and sodium hydrate, would be doubtless correct were carbon monoxide the principal product formed in the latter reaction. That it may be formed appears not improbable, since we know that Geuther\* noticed its formation by the action of a dilute alcoholic solution of potassium hydrate on chloroform. But this view is also open to serious objections: firstly, the formation of carbon monoxide in the reaction of Reimer could hardly have escaped notice; secondly, the amount of carbon monoxide, if formed, would not justify the yield obtained of aldehydes; and finally, numerous attempts to obtain salicylic aldehyde by the action of free as well as nascent carbon monoxide have not succeeded.

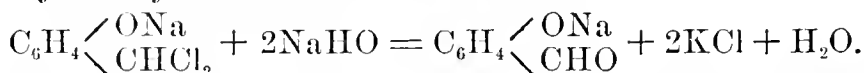
There is still an hypothesis which appears to me to explain the reaction in question more satisfactorily, than those we have just considered. The action of an aqueous solution of sodium hydrate on chloroform proceeds very slowly, even on boiling. We have, however, in sodium hydrate a compound which possesses a strong affinity for chlorhydric acid, and we

\* Ann. Chem. Pharm. 123, 121.

can easily understand that the alkali should extract the component parts of chlorhydric acid from sodium phenolate and chloroform; the hydrogen can, of course, only come from the benzene nucleus of the phenolate:



The compound first formed is, therefore, sodium oxybenzylidenchloride, the salt of a compound discovered by L. Henry,\* and this salt is doubtless soluble in the solution in which it is formed. We know, however, that benzylidenchloride in an alcoholic alkaline solution is easily converted into benzoic aldehyde,† and there is no reason to doubt that sodium oxybenzylidenchloride under the influence of the excess of sodium hydrate employed in the reaction would undergo a like decomposition, thus forming the sodium salt of an oxy-aldehyde and sodium chloride:



It is easy to mention well-characterized reactions which bear a strong analogy to the reaction of Reimer, when it is considered in this light. For instance, the formation of the compound  $\text{C}_6\text{H}_5\text{—PCl}_2$  by the action of phosphorus trichloride on benzene‡ resembles the first step, and that this compound yields on contact with water  $\text{C}_6\text{H}_5\text{P(OH)}_2$ , corresponds with the second step of the Reimer reaction. Again, the formation of triphenylmethane by the action of aluminium chloride on a mixture of chloroform and benzene is similar. The first step of this is doubtless the formation of benzylidenchloride; and were this compound formed in the presence of an alcoholic alkaline solution, or even, perhaps, a metallic oxide, benzoic aldehyde would probably be formed. It is hardly necessary to call attention to the fact that the hydrogen atoms in the nucleus of phenol show a much greater reactive power than those of benzene, and that the conditions under which the formyl group is introduced, by the action of sodium hydrate and chloroform on phenol, are especially favorable for this reaction.

The results obtained by Reimer and Tiemann§ by the action of sodium hydrate and chloroform on para-oxybenzoic acid

\* Ber. d. chem. Gesell. 1869, 135.

† Compt. rend. 56, 222.

‡ Ann. Chem. 181, 265.

§ Ber. d. chem. Gesell. 1876, 1286.

are extremely interesting. We have seen that the formyl group has a tendency to substitute in phenol, the hydrogen atoms occupying in the nucleus the ortho- and para-positions towards the hydroxyl group. Reimer and Tiemann obtained from para-oxybenzoic acid orthoformyl-para-oxybenzoic acid and para-oxybenzoic aldehyde, the latter compound being formed by the substitution of the carboxyl of para-oxybenzoic acid by the formyl group. Reimer and Tiemann direct attention to the formation of aldehydes by the distillation of the calcium salts of organic acids with calcium formate, and consider this reaction as an analogous instance of the substitution of a carboxyl by the formyl group. But this reaction may be explained in a different manner, and according to which the analogy between the two instances in question disappears:

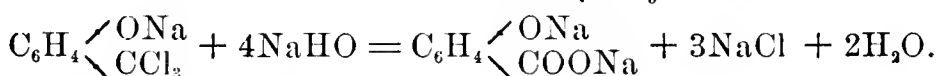
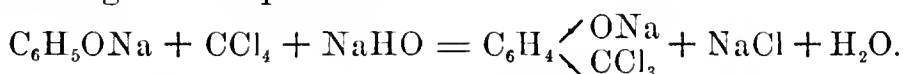


The reaction as expressed by II. is, I believe, the common acceptance, and is the most probable. For instance, according to I. we must suppose that the bond between two carbon atoms is broken in order that one of these atoms should be subsequently joined with a different carbon atom. To explain the formation of para-oxybenzoic aldehyde in the present instance, we may suppose that chloroform, with its tendency to enter in the para-position towards the hydroxyl group of phenol, acts on the sodium atom of the COONa group, forming at first the compound  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{ONa} \\ \diagdown \text{COO} - \text{CHCl}_2 \end{array}$ , which is then decomposed by sodium hydrate into sodium chloride and  $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{ONa} \\ \diagdown \text{COO} - \text{CHO} \end{array}$ . This compound, owing to the negative character of the group  $-\text{COO} - \text{CHO}$ , is unstable towards bases, they absorbing that part for which they have the greatest affinity, and which is carbonic acid, thus leaving the formyl group.

Finally, Reimer and Tiemann\* found that by the action of carbon tetrachloride on an alcoholic solution of sodium hydrate and phenol a mixture of ortho- and para-oxybenzoic acids was

\* Ber. d. chem. Gesell. 1877, 1285.

formed. This reaction, in forming the ortho- and para-acids by the use of sodium hydrate, shows clearly that it is not due to the previous formation of carbonic acid, since otherwise only the ortho-acid would have been obtained. The reaction may be explained in a similar manner to the chloroform-aldehyde reaction, the sodium hydrate extracting chlorhydric acid according to the equation:



BUFFALO, Nov. 8th, 1879.

## ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

### IV.—ON THE OXIDATION OF ORTHOTOLUENESULPHAMIDE.

BY IRA REMSEN AND C. FAHLBERG.

Some years ago\* in the course of an investigation on the oxidation of the sulphonic acids derived from toluene, one of us (R) attempted to convert orthotoluenesulphonic acid into orthosulphobenzoic acid. The analogous transformation in the para-series takes place very easily, both with chromic acid and permanganate of potassium. It was at that time shown that in the ortho-series chromic acid, as in other similar cases, fails to effect the desired oxidation. Attention was turned to the permanganate, but definite results were not reached, as is indicated by these words, quoted from the original paper: "It is possible that other oxidizing agents, as for instance potassium permanganate, may yield more satisfactory results. A preliminary experiment made with this salt in an alkaline solution showed that oxidation took place readily; and I shall soon commence the study of this reaction in detail."

\* Amer. Jour. Sci. and Arts, v. 179, 274, 354; and Ann. der Chemie. 178, 275.

Numerous circumstances have prevented until the present the fulfilling of the promise here made. In the meantime one of the chief reasons for desiring the preparation of ortho-sulphobenzoic acid has lost much of its importance. It was at first hoped that, just as the meta- and para-acids can be converted into the corresponding phthalic acids by means of Victor Meyer's reaction, the ortho-acid might yield ortho-phthalic acid; and, as at that time no direct passage from a toluene derivative to phthalic acid was known, the importance of the hoped-for transformation will be readily recognized. Somewhat later Weith\* succeeded in oxidizing orthotoluic acid by means of potassium permanganate in alkaline solution, and thus orthosulphobenzoic acid was robbed of much of the interest previously connected with its existence. We have nevertheless undertaken the investigation of the phenomena observed in connection with the oxidation of orthotoluenesulphamide, a complete understanding of these being necessary as a foundation for the series of investigations which have been in progress for some time in the laboratory of this University. The results of the investigation proved to be more than usually interesting as the description will show.

*Preparation of Orthotoluenesulphamide.*

Two and a half pounds of pure toluene, boiling at 111-112°, were treated with fuming sulphuric acid until the toluene was completely dissolved. By means of the usual reactions the sulphonic acids thus obtained were converted into the corresponding chlorides, and these were first thoroughly washed with water at the ordinary temperature. The mixed chlorides were now brought upon an asbestos filter and the liquid drawn off as completely as possible by means of a filter-pump. Cold water was finally drawn through the solid mass on the filter until the filtrate ceased to appear oily. The liquid chloride was now separated from the wash-water and cooled down to -15° C. Some of the solid again separated, and this was filtered off as above described. The liquid filtrate was very nearly pure orthotoluenesulphochloride. This, by treatment with ammonia, yielded an amide which after one

\* Ber. d. chem. Gesell. vii, 1057.

crystallization fused at  $153\text{--}154^\circ$ , *i. e.*, the fusing point of pure orthotoluenesulphamide. The amide was converted into salicylic acid by fusing it with potassium hydroxide, and not a trace of paraoxybenzoic acid was formed at the same time. An analysis was made of the amide, which gave 18.72 per cent. sulphur, while the formula requires 18.71 per cent. sulphur.

*Formation of Benzoic Sulfinide.*

A small portion of the amide was treated with a solution of permanganate of potassium, and, as oxidation was seen to take place readily, the process was undertaken on a larger scale. The following proportions were found to yield satisfactory results: 10 grams of the amide and 40 grams of permanganate dissolved in 1 litre of water. This mixture was heated from eight to ten hours on a water-bath. The excess of permanganate was reduced by a few drops of alcohol, and the insoluble manganese compounds filtered off. The perfectly colorless filtrate was evaporated down to about 200 c. c. and again filtered. After cooling, hydrochloric acid was added and a precipitate was formed. This was easily obtained perfectly pure by recrystallization from water. As it exhibited all the properties of a chemically pure substance, it was analyzed.

I. 0.26245 gram substance gave 0.33655 gram  $\text{BaSO}_4$  = 0.0462 gram S.

II. 0.2344 gram substance gave 0.2964 gram  $\text{BaSO}_4$  = 0.0407 gram S.

III. 0.206 gram substance gave 0.2651 gram  $\text{BaSO}_4$  = 0.0364 gram S.

IV. 0.2493 gram substance gave 16.9 c. c. N, at  $15^\circ$  at 761 m. m. Barom. = 0.019807 gram N.

		Calculated.		Found.			
				I.	II.	III.	IV.
$\text{C}_7\text{H}_5\text{O}_3$	...	137	74.86	...	...	..	...
N	...	14	7.65	...	...	...	7.94
S	...	32	17.49	17.61	17.40	17.67	...
		183	100.00				

Accordingly, the empirical formula of the product is

$C_7H_5O_3NS$ , whereas the formula of the sulphamine acid, the formation of which was looked for, is,  $C_7H_7O_4NS$ , or  $C_6H_4 \begin{smallmatrix} \diagup SO_2NH_2 \\ \diagdown CO_2H \end{smallmatrix}$ . The calculated percentages of sulphur and nitrogen in the latter substance are 15.92 per cent. sulphur and 6.97 per cent. nitrogen. Instead then of obtaining the normal sulphamine acid, as in the case of the corresponding para-compound, we obtained a product which differs from the sulphamine acid in that it contains a molecule of water less. It is a sort of anhydride, or a condensation-product, in which the groups  $CO$  and  $SO_2NH$  are probably connected as represented in this formula:  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown SO_2NH \end{smallmatrix}$ , which is certainly the simplest that can be suggested.

Similar condensation-products are known in considerable numbers, and they are almost entirely confined to the ortho-series, though a few examples are known which indicate the possibility of their formation in the isomeric series. The kind of grouping represented in the above formula is, to a certain extent, the characteristic feature of some of the compounds allied to indigo. In these we have, in all probability, a carboxyl and an amido group united as in our new product, but there are some differences in the conditions which are suggestive.

In isatine, for instance, we have the group  $\begin{smallmatrix} -CO.CO \\ | \\ -NH \end{smallmatrix}$  taking

the place of two hydrogen atoms in the benzene nucleus, whereas in the new product under consideration the complex

group  $\begin{smallmatrix} -CO \\ | \\ -SO_2.NH \end{smallmatrix}$  plays a similar part. It is well known that

the groups  $CO_2H$  and  $NH_2$  can exist in the ortho-position with reference to each other in the benzene nucleus, ortho-

amidobenzoic acid  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown NH_2 \end{smallmatrix}$  being a stable compound. If,

however, either the carboxyl group be removed from direct connection with the nucleus, as in the case of isatine through the intervention of the group  $CO$ , or the amido group be similarly removed, as in the case of our product through the intervention of the group  $SO_2$ , then the peculiar condensation takes place. Whatever the character of the influence may be

which is exerted upon the groups directly connected with the benzene nucleus, and which prevents the formation of the condensation-product from orthoamidobenzoic acid, it is thus seen that this influence is not conveyed through the groups CO and SO<sub>2</sub>.

In our first notice concerning this investigation\* the name *anhydroorthosulphaminebenzoic acid* was proposed for the condensation product. The only serious objection to this name is its length. As other similar products have since been discovered in this laboratory, it seems now desirable to devise a shorter generic name for this class of compounds. The characteristic feature of these compounds is the presence in

them of the group  $\begin{array}{c} \text{— CO} \\ | \\ \text{— SO}_2\text{NH} \end{array}$ . We propose to designate all

compounds which contain this group as *sulfinides*, and, as they always correspond to some carboxyl derivative, to use the name of the latter to specify the particular sulfinide to be defined. Thus, the compound with which we are now concerned corresponds to, or is, in a certain sense, a derivative of benzoic acid. Hence its full name would, according to this principle of nomenclature, be *benzoic sulfinide*. A compound bearing the same relation to toluic acid can be imagined. Its

formula would be  $\text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{CO} \\ \text{— SO}_2\text{NH} \\ \diagdown \text{CH}_3 \end{array}$ , and its name toluic sulfinide.

Compounds of a similar nature bearing the same relation to isophthalic and terephthalic acids have actually been prepared. These may be called isophthalic and terephthalic sulfinide.

*Benzoic sulfinide* (or anhydrosulfaminebenzoic acid) is difficultly soluble in cold water. It is much more soluble in hot water, and can be obtained in crystallized form from its aqueous solution. It crystallizes in short thick prismatic forms, which are not well developed. Alcohol and ether dissolve it very easily. It fuses at 220° (uncorr.), but undergoes at the same time partial decomposition. It possesses a very marked sweet taste, being much sweeter than cane-sugar. The taste is perfectly pure. The minutest quantity of the substance, a bit of its powder scarcely visible, if placed upon the tip of the tongue, causes a sensation of pleasant sweet-

\* Ber. d. chem. Gesell. xii. 469.

ness throughout the entire cavity of the mouth. As stated above, the substance is soluble to only a slight extent in cold water, but if a few drops of the cold aqueous solution be placed in an ordinary goblet full of water, the latter then tastes like the sweetest syrup. Its presence can hence easily be detected in the dilutest solutions by the taste. Orthonitrobenzoic acid has this same property, but the sweetness is by no means as intense as in the case of benzoic sulfinide.

Fused with potassium hydroxide, benzoic sulfinide is converted completely into pure salicylic acid. The reaction is a perfect one, the salicylic acid being obtained immediately in pure condition.

Phosphorus pentachloride does not act upon benzoic sulfinide either at the ordinary temperature or when heated. These facts indicate, of course, that the substance contains, as represented in the formula, no hydroxyl. Attempts were made to prepare the ethyl ester by passing dry hydrochloric acid gas into the alcoholic solution, but mostly without success. In nearly every case the unchanged sulfinide was obtained in undiminished quantity. It was found, however, that the sulfinide is more difficultly soluble in alcohol containing hydrochloric acid than in pure alcohol, for, after hydrochloric acid was conducted for some time into the dilute alcoholic solution, the original substance separated in crystalline form. This separation was not due to evaporation of the alcohol, as was determined by separate experiments.

In aqueous solution benzoic sulfinide has the properties of an acid. By neutralizing the solution with various carbonates corresponding salts were obtained, and these had the composition of salts of sulphaminebenzoic acid,  $C_6H_4 \begin{smallmatrix} \diagup CO_2H \\ \diagdown SO_2NH_2 \end{smallmatrix}$ . Strong acids throw down from solutions of these salts benzoic sulfinide, and not sulphaminebenzoic acid. We have not succeeded in obtaining the acid itself in free condition, and it hence appears probable that it is not capable of existence.

*Barium Orthosulphaminebenzoate,*

$(C_6H_4 \begin{smallmatrix} \diagup SO_2NH_2 \\ \diagdown CO_2 \end{smallmatrix})_2Ba + 4\frac{1}{2}H_2O$ , was prepared by treating the aqueous solution of benzoic sulfinide with barium carbonate.

It is easily soluble in cold and hot water, but crystallizes from a concentrated solution in lustrous needles, concentrically arranged. By long standing in contact with the air it effloresces, and contains then only 9.02 per cent. or three molecules of water. It is soluble with difficulty in alcohol. It was analyzed with the results here given:

I. 0.2571 gram substance lost at  $170^{\circ}$  0.0331 gram  $\text{H}_2\text{O}$  = 12.87 per cent.  $\text{H}_2\text{O}$ .

II. 0.2455 gram substance gave 0.094 gram = 0.0552 gram Ba = 22.51 per cent. Ba.

		Calculated.		Found.	
				I.	II.
$(\text{C}_7\text{H}_6\text{O}_4\text{SN})_2$	...	400	64.72	...	...
Ba	...	137	22.17	22.51	...
$4\frac{1}{2}\text{H}_2\text{O}$	...	81	13.11	...	12.87
		<hr/>	<hr/>	<hr/>	<hr/>
		618	100.00		

*Magnesium Orthosulphaminebenzoate,*

$(\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}_2 \\ \diagdown \text{SO}_2\text{NH}_2 \end{smallmatrix})_2 \text{Mg} + 6\frac{1}{2}\text{H}_2\text{O}$ , prepared like the barium salt, crystallizes from concentrated solutions in long, transparent, hard needles. It is easily soluble in water. It crystallizes from its solution in ordinary alcohol (94 per cent.) with the same quantity of water of crystallization as it does from water. It is more difficultly soluble in alcohol than in water, and can best be obtained pure by crystallization from alcohol.

I. 0.1646 gram of the salt, crystallized from after being dried by lying in the air, lost 0.03525 gram  $\text{H}_2\text{O}$  at  $180^{\circ}$  = 12.41 per cent.  $\text{H}_2\text{O}$ , and gave 0.0396 gram  $\text{MgSO}_4$  = 4.81 per cent. Mg.

II. 0.196 gram substance, crystallized from alcohol, lost 0.0425 gram  $\text{H}_2\text{O}$  = 21.68 per cent.  $\text{H}_2\text{O}$ , and gave 0.0475 gram  $\text{MgSO}_4$  = 4.70 per cent. Mg.

		Calculated.		Found.	
				I.	II.
$(\text{C}_7\text{H}_6\text{O}_4\text{SN})_2$	...	400	73.94	...	...
Mg	...	24	4.44	4.81	4.70
$6\frac{1}{2}\text{H}_2\text{O}$	...	117	21.62	21.41	21.68
		<hr/>	<hr/>	<hr/>	<hr/>
		541	100.00		

*Lead orthosulphaminebenzoate* forms a syrupy mass which even after long standing does not solidify.

The *potassium, sodium and ammonium salts* are very easily soluble in hot and cold water and alcohol. They crystallize in needles from very concentrated aqueous and alcoholic solutions.

The salts of the heavy metals, as far as they were examined, do not crystallize well. All the salts prepared by us have the sweet taste which is characteristic of the acid itself. The effect upon the organs of taste is instantaneous in the case of the magnesium and barium salts which are more easily soluble than the sulfinide itself. In the case of the sulfinide, which is difficultly soluble, an appreciable amount of time intervenes between the application to the tongue and the sensation of sweetness.

As stated above, it was found difficult to prepare the ethyl ester from the sulfinide by treating the alcoholic solution with hydrochloric acid. When very strong alcohol and perfectly dry hydrochloric acid are used, an oily substance is formed which can be precipitated by water from the alcoholic solution. This, though it was not analyzed, we take to be the ethyl ester. It is soluble in boiling water and separates as an oil on cooling. It has the sweet taste characteristic of the sulfinide.

#### *Orthosulphobenzoic Acid.*

When the filtrate from benzoic sulfinide, precipitated directly after the completion of the oxidation, is further evaporated to about 75 c. c. and then allowed to stand, a potassium salt is deposited in well-formed crystals. This was separated by recrystallization from a little potassium chloride which was at first deposited with it, and was then perfectly pure. The separation from the sulfinide is very simple in consequence of the great difference in solubility of the two substances. The separation from potassium chloride requires two or three recrystallizations. The qualitative analysis of the salt showed that it contained potassium but *no nitrogen*; and, further, that the salt still possessed acid properties, indicating that it is derived from a polybasic acid. The quantitative analyses gave these results:

I. 0.2700 gram salt gave 0.097 gram  $K_2SO_4 = 0.0435$  gram K.

II. 0.236 gram salt gave 0.2365 gram  $\text{BaSO}_4 = 0.03248$  gram S.

The salt contains no water of crystallization.

		Calculated.		Found.	
$\text{C}_7\text{H}_5\text{O}_5$	...	169	70.39	...	...
K	...	39.1	16.28	16.13	...
S	...	32	13.33	...	13.75
		<hr/>	<hr/>	<hr/>	<hr/>
		240.1	100.00		

The figures obtained correspond to those required by the formula of *mono-potassium sulphobenzoate*,  $\text{C}_6\text{H}_4\text{SO}_3\text{K}\text{CO}_2\text{H}$ . It was shown that the salt belongs to the ortho-series by fusing it with potassium hydroxide. The only product was salicylic acid, and the yield in this was quantitative. The absence of nitrogen, the acid properties, the results of the analyses and the formation of salicylic acid prove conclusively the nature of the salt.

Mono-potassium orthosulphobenzoate,  $\text{C}_6\text{H}_4\text{SO}_3\text{K}\text{CO}_2\text{H}$ , is precipitated in crystalline form from a concentrated solution of the neutral salt on the addition of hydrochloric acid. Recrystallized from water, it is deposited in beautiful, large, transparent plates, which appear to be monoclinic.

Dr. J. R. McD. Irby had the kindness to examine the salt crystallographically, and we are indebted to him for the following statement of his results:

"System rhombic,  $a : b : c = 1.4688 : 1 : 1.8129$ .

Forms  $\{001\}$   $\{111\}$   $\{101\}$ .

$001 \vee 111 = * 65^\circ 29\frac{2}{3}'$  mean of 9 values from  $65^\circ 22'$  to  $38'$ .

$111 \vee \bar{1}\bar{1}\bar{1} = * 97^\circ 33'$  mean of 5 values from  $97^\circ 27'$  to  $42'$ .

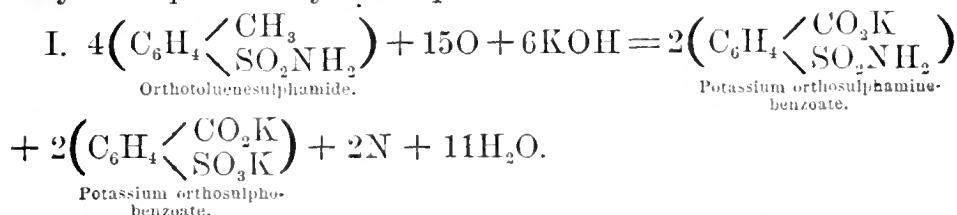
	Calculated.	Observed.
$101 \vee 001$	$50^\circ 59\frac{1}{2}'$	$51^\circ 3'$ mean.

$111 \vee \bar{1}\bar{1}\bar{1}$	$61^\circ 44\frac{1}{3}'$	$61^\circ 43'$ mean.
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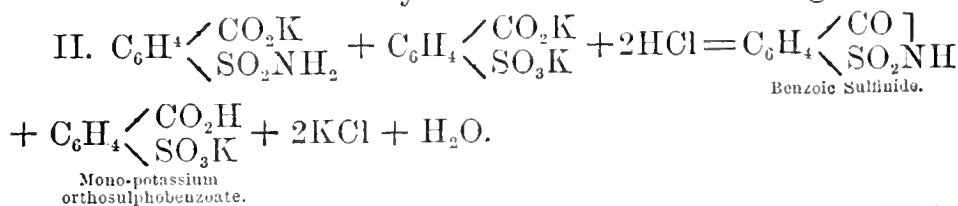
"Form of crystals, thin rhombic plates with edges bevelled by  $\{111\}$ .  $\{101\}$  occasionally terminates the macro-edge of  $\{111\}$ . A perfect cleavage is parallel to  $\{001\}$ ."

Orthosulphobenzoic acid is by no means a secondary product in the oxidation of orthotoluenesulphamide. From 10

grams of the amide there were obtained 5 grams of the sulfinide (dried after the first precipitation and then weighed before recrystallization) and 4 grams of the acid potassium salt. As, however, the salt is much more easily soluble in water than the sulfinide, and hence cannot be as thoroughly separated from its solutions, it seems fair to conclude that the two products of oxidation are formed in about equal quantities, probably in quantities which are proportional to their molecular weights. In other words, from two molecules of orthotoluenesulphamide there are probably formed one molecule of benzoic sulfinide and one molecule of orthosulphobenzoic acid. Both bodies are present in the oxidizing liquid in the form of potassium salts. On the addition of hydrochloric acid benzoic sulfinide is thrown down, while the neutral potassium salt of orthosulphobenzoic acid is converted into the acid salt. The question as to what becomes of the nitrogen which leaves the amide cannot be positively answered as yet. It was shown that ammonia is not formed. If we assume that it passes off in the form of free nitrogen, the oxidation may be expressed by this equation:



Then on the addition of hydrochloric acid these changes occur:



In order to determine whether orthosulphobenzoic acid is formed as a direct product of the oxidation process, or indirectly by the action of hydrochloric acid on the potassium salt of sulphaminebenzoic acid, a small quantity of the latter was evaporated on the water-bath with hydrochloric acid. It remained completely unchanged. Further, instead of evaporating at once the liquid from the manganese precipitate after the oxidation, hydrochloric acid was first added and the liquid then evaporated. The result was exactly the same as

in the case first studied and described, so that we are forced to conclude that orthosulphobenzoic is in reality a product of oxidation of the sulphamide.

The formation of sulphobenzoic acid by oxidation of toluene-sulphamide is analogous to the formation of sulphisophthalic acid in the oxidation of sulphaminemetatoluic acid.\* In both cases the sulphamine-group is converted into the sulpho-group, while, at the same time, a methyl-group in the ortho-position in the original compound is converted into carboxyl. In both cases, too, under certain circumstances, two products are formed, one containing nitrogen, the other containing none.

When benzoic sulfinide is heated in a sealed tube to  $150^{\circ}$  with concentrated hydrochloric acid, it is converted by a perfectly clean reaction into orthosulphobenzoic acid. We did not succeed in replacing the sulpho-group by hydrogen. Parasulphaminebenzoic acid conducts itself in the same way. Pure parasulphobenzoic acid was obtained and recognized through its characteristic acid barium salt. The latter was analyzed and gave 23.31 per cent. Ba, the formula,  $(\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{SO}_3 \end{smallmatrix})_2\text{Ba} + 3\text{H}_2\text{O}$ , requiring 23.10 per cent. Ba.

*Orthosulphobenzoic acid*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{SO}_3\text{H} \end{smallmatrix}$ , crystallizes from very concentrated aqueous solutions in beautiful, large plates which resemble in appearance the acid potassium salt above described. It fuses at  $240^{\circ}$ , at the same time undergoing decomposition. The acid is not deliquescent and can be kept in the air without undergoing change. It is very easily soluble in cold as well as hot water. Alcohol dissolves it only in small quantity, ether not at all.

*Acid Barium Orthosulphobenzoate,*

$(\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{SO}_3 \end{smallmatrix})_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ , was obtained from the easily soluble neutral salt by adding hydrochloric acid. It crystallizes in needles which resemble those of the corresponding salt of parasulphobenzoic acid, but it is much more easily soluble in water than the para-salt. Like the latter, as well

\* This Journal, 1, p. 121.

as the meta-salt, it does not give up all its water of crystallization below  $200^{\circ}$ . It is partially decomposed at  $250^{\circ}$ . The analysis gave these results:

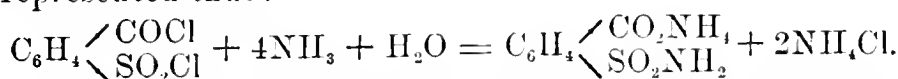
0.287 gram air-dried salt lost 0.0238 gram  $\text{H}_2\text{O}$  at  $200^{\circ}$ , and gave 0.1155 gram  $\text{BaSO}_4 = 0.0679$  gram Ba.

		Calculated.		Found.
$(\text{C}_7\text{H}_5\text{O}_3\text{S})_2$	...	402	68.84	...
Ba	...	137	23.46	23.66
$2\frac{1}{2}\text{H}_2\text{O}$	...	45	7.70	8.28
		584	100.00	

For the purpose of comparison the *acid potassium salt* was prepared from pure orthosulphobenzoic acid. It was found to be identical in every respect with the salt described above and obtained by direct oxidation from toluenesulphamide.

Just as benzoic sulfinide can be easily transformed into orthosulphobenzoic acid, so the reverse process is also a simple one. It is only necessary to treat the neutral potassium salt of orthosulphobenzoic acid with phosphorus pentachloride, which in all probability gives rise to the formation of the normal chloride. When the chloride is treated with strong aqueous ammonia complete solution follows and, even after long standing, nothing separates. If the solution be evaporated to a small volume, the inorganic salts begin to crystallize out first. If, however, the solution be treated with hydrochloric acid, benzoic sulfinide is precipitated.

The explanation of these reactions is probably this. When the chloride is treated with ammonia, it is converted into the ammonium salt of orthosulphaminebenzoic acid, instead of into the normal amide. The addition of hydrochloric acid then causes the precipitation of benzoic sulfinide, as it does from the solution of any other salt of the sulphamine acid. The formation of the ammonium salt from the chloride may be represented thus:



This transformation of an orthobibasic acid into the corresponding *imide* compound by successive treatment with phosphorus pentachloride, ammonia and hydrochloric acid suggests

the possibility of transforming other bibasic acids of the ortho-series in the same way. At the suggestion of one of us (R), Mr. Kuhara has undertaken the study of this reaction in connection with phthalic acid, and has already succeeded in converting phthalic acid into a beautifully crystallized substance, the analyses of which indicate that it is the imide,  $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ CO \end{smallmatrix} > NH$ . Its properties, however, are quite different from those ascribed to phthalimide by Laurent. Other acids will be taken up in due time.

Finally, an attempt was made to convert orthosulphobenzoic acid into phthalic acid by means of the reaction with sodium formate. Equal parts of the formate and potassium orthosulphobenzoate were heated together carefully according to the directions of V. Meyer. The mass was dissolved in water and decolorized with animal charcoal. On being treated with hydrochloric acid it became turbid. It was repeatedly shaken with ether, and the ether evaporated from the extract. When the mass was dissolved in a little hot water and the solution cooled a crystalline substance separated. This was, however, not phthalic acid, for it did not fuse until a very high temperature was reached, and then it underwent decomposition and gave off, among other things, sulphuretted hydrogen. In all probability the body is similar to the one obtained by Ador in the preparation of isophthalic acid from metasulphobenzoic acid. The product was not examined further, as the quantity in our possession was very small.\*

January, 1880.

## ON AN UNUSUAL CASE OF ELECTROLYSIS.

By J. W. MALLET.

A galvanic battery of six couples, of Smee's construction, the flat rectangular plates about 15 by 7 centimeters, was frequently used, in connection with an induction coil, for

\* Dr. Fahlberg is engaged in the study of certain other phenomena similar to those described in this paper. He will soon communicate his results to this Journal for publication.

lecture-table purposes. When not required in action the plates, all attached to the same wooden frame, were raised from the divided stoneware trough by cords wound upon an axle, and kept suspended above the acid by means of a ratchet-wheel and pawl. The two terminal copper wires were generally coiled loosely together, so as to be out of the way, when the battery was thus set aside.

On one occasion the apparatus was carried from the lecture-table to an adjoining room, the plates having been raised out of the acid, and it remained unnoticed for two or three days, when I perceived that the pawl had slipped from its place and the plates had fallen down and were fully immersed in the acid liquid—originally consisting of about one part, by weight, of sulphuric acid to seven or eight of water, but to which some additional strong acid had afterwards been added by pouring directly into the cells when, during a lecture, the action was found insufficient, the apparatus having been used at intervals for some time. This additional acid was not accurately weighed or measured, but was poured in, as far as could roughly be guessed by the eye, in equal quantity into each cell. On emptying the trough and washing off the plates, those of zinc were found much corroded, and it was noticed that one of the sheets of thin platinized silver-foil lying between them was quite stiff and very considerably thickened. Detaching it from the rest—it belonged to the third cell from one end or fourth from the other—I found that the surface on both sides was thickly coated with metallic zinc. By immersing it in pure dilute sulphuric acid in a beaker 14.813 grm. of zinc was removed, and then, the solution taking place slowly, connection was made with the negative pole of a small galvanic battery, and an insoluble opposite electrode from the positive pole immersed in the same beaker of acid, when 15.762 grm. more was removed; so that, the silver foil being now clean, 30.575 grammes altogether of zinc had been taken from its surface.

Obviously the condition of the liquid had not been quite the same in all the divisions of the trough, the acid having been of different strength; doubtless, as the plates lay neglected in it, it had first become completely converted into zinc sulphate in this particular cell, in which subsequently, the circuit being

closed by the loose contact of the terminal wires, the chemical action of the battery had transferred itself from hydrogen sulphate to zinc sulphate, this becoming a "decomposing cell," and metallic zinc was electrolytically thrown down from the strong solution of its salt.

Although the explanation of the fact is simple enough, its actual occurrence is new to me. Such an accident may have often been observed, very probably by telegraph-operators or electro-platers, but, if so, I have never seen any notice of it. It seems therefore worth a passing mention.

UNIVERSITY OF VIRGINIA, *Jan.* 24, 1880.

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## REVIEWS AND REPORTS.

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### BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(Continued from page 361.)

#### MINOR CHEMICAL MANUFACTURES.

##### *Inorganic Chemicals.*

*Iodine.*—The chief event in the recent history of iodine production has been the utilization of the mother-liquors from which Chilian sodium nitrate has been crystallized. Cupric sulphate and sodium sulphite being added to the liquid, cuprous iodide is precipitated, and this, for the most part shipped to Europe, is afterwards decomposed by sulphuretted hydrogen or by zinc, and converted into an alkaline iodide; to a less extent the solutions are treated with a regulated quantity of sodium sulphite alone, and the iodine collected as such either by precipitation or distillation. Kelp has until lately remained the most important source of supply, although this material is worked at a serious disadvantage since its potassium and sodium salts have had to bear in the market the competition of the products of Stassfurt industry and the greatly extended Leblanc process. Large loss of iodine is known to occur in burning to kelp the sea-weeds exposed to atmospheric oxygen,

but the attempt to remedy this by charring in close vessels instead of burning, utilizing afterwards the volatile products, seems to have failed of success from the unwieldy mass of crude sea-weed requiring transportation to the seat of such manufacture. The rapid increase of demand, and consequently of price, for iodine, caused by its extensive use in making sundry of the coal-tar colors, notably the violets and greens, has been followed by a partial falling off, due to the efforts to substitute in this application other salts for the iodides of the alcohol radicles. The problem of finding means, physical or chemical, for obtaining directly from sea-water the minute amount of iodine it contains seems still perhaps worthy of consideration.

*Potassium Iodide.*—The medicinal use of this salt continually increases the scale upon which its production is required, while the statistics of photography show a still more rapid increase of the demand for it wherever civilized man is to be found. A recent paper by E. Schering discusses the different methods employed for making it, of which on the whole that which seems most generally in use is the solution of iodine in aqueous potassium hydrate, evaporation to dryness with addition of charcoal powder, and ignition to destroy the iodate formed; Schering himself, however, giving the preference to the production of iron iodide and decomposition by potassium carbonate.

*Bromine.*—It is but a short time since this was but a rare laboratory chemical; now it is manufactured by tens, nay hundreds of thousands of pounds annually, and its production upon a still larger scale is prevented merely by the low price which it commands at present. Formerly obtained only from the "bittern" of sea-water evaporation, and in a very small way from kelp, the two new sources of supply which have proved so much more extensively available are the mother-liquors obtained at Stassfurt in working the salts of potassium and magnesium, and those produced in salt-boiling in Ohio, West Virginia and Pennsylvania. One can hardly believe that new and important uses will not yet be found for this potent reagent, now mainly devoted to the production of potassium bromide, the employment of which in medicine upon a very large scale is the result of but a few years experience. The substitution of bromine for iodine alcoholic compounds in the manufacture of the coal-tar dyes was at one time eagerly attempted, then pronounced unsatisfactory, but has again, in modified form, come to some extent into use, while bromine derivatives of the hydrocarbons and phenols have played some part in the development of other branches of the industry of artificial dye-stuffs, especially of late in the production of eosine and other resorcline derivatives. It seems really desirable that a careful test shall be made of the

economy with which bromine may be substituted for chlorine in the application of Plattner's process, simplified, to saving gold from the "tailings" and "beach-sands" of the Pacific States. It does not appear impossible that such an application might be combined with arrangements for recovering at least the greater part of the bromine, but even without this, there are probably localities at which the method might be profitably used.

There is little new in the comparatively simple processes by which bromine is at present made. Some ingenuity has been shown, however, in devising the means for avoiding danger and annoyance in the transportation of so active and volatile a substance; for example, it has been shipped, when not at once made into potassium bromide, as bromide of iron, and of ethyl, in harmless solid and liquid form.

*Phosphorus*—In view of the small reason for making at the present day any special mystery of this manufacture, it is a little remarkable how difficult it is to obtain accurate information as to its details; probably the chief cause of this is the concentration of the manufacture in the hands of a very few firms. It is said that mineral phosphates, the so-called coprolites, Redonda guano, &c., have largely, if not for the most part, replaced bone-ash as the crude material used. It is reported, too, that instead of limiting the action upon this of sulphuric acid to the removal of two-thirds only of the calcium, all is removed as calcium sulphate, and syrupy phosphoric acid, dried up with charcoal powder, constitutes the material submitted to distillation. The suggestion made long ago by Wœhler, to dispense altogether with the use of sulphuric acid, and procure phosphorus by distilling a mixture of calcium phosphate, silica and carbon, is said to have been adopted upon an industrial scale some years since in France, but whether successfully and persistently may be doubted—the very high temperature necessary for fairly complete decomposition of the phosphate is a serious drawback. The failure of amorphous phosphorus to replace the ordinary variety in the manufacture of all friction matches has not arrested the production of the former on the large scale. In making matches the much more ready inflammability of common phosphorus causes it to be most extensively employed, but use is made of the amorphous form of the element to some extent for matches, and for the surfaces upon which "safety matches" are ignited, as well as under circumstances which make its more manageable chemical activity advantageous, as in making the haloid compounds of ethyl and methyl for the production of the aniline dyes. A new field for the use of phosphorus in metallurgy has been opened up by the introduction of phosphor-bronze, already referred to in this report.

*Carbon disulphide*.—This substance, possessing special value

as a solvent, has been an article of manufacture in a large way for but a moderate number of years. The scale upon which it is made has rapidly increased, but has been hardly kept pace with by improvement in the method used and in economy of result. Iron retorts have been substituted for those of clay formerly in use, and the practice has been introduced of distilling over the sulphur and bringing it into the retort in the form of vapor to act upon the red-hot carbon. The iron of the retorts is attacked and gradually converted into sulphide; although the walls are made thick enough to last for a considerable time, it seems likely that additional durability might be gained by washing over the inside surface with a moderately fusible glaze, as of borax and clay. The product is refined with much greater care than formerly, so that much of that to be found in commerce is almost quite free from the very nauseous odor belonging to the crude liquid first condensed. A large amount of free sulphur being carried over with the sulphide, having afterwards to be separated in the refining process, it would seem well to transmit the mixed vapors from the first retort through a second, or even a third, cylinder of glowing carbon before carrying them off to the condensing apparatus.

Used at first almost solely by the manufacturers of india-rubber, carbon disulphide has acquired greatly increased importance as furnishing the means of dissolving out fats and oils from various materials which could not be treated, or could not be treated with equal advantage, in any other way. Thus from oil-seed cakes, from the marc of olive oil pressing, from woolen rags and waste, from cotton waste used in wiping machinery and packing stuffing-boxes and axles, and from bones from which gelatine and phosphates are afterwards to be made, large quantities of fat are recovered. To a limited extent the same solvent has been brought into use to collect sulphur from poor "sulphur-stone," and to extract delicate perfumes and the aromatic ingredients of spices and condiments. For all these purposes a rival has appeared in the shape of the more volatile portions of petroleum, forming the so-called petroleum spirit or petroleum naphtha. The abundant supply of this at a very cheap rate has tended for a few years past to check the extension of the carbon disulphide manufacture. A new and special use for the latter has, however, quite lately grown up in its application as such, as well as of the *sulpho-carbonates*, as the means of checking the ravages of the *phylloxera* in European, especially French, vineyards. Later the ethyl- and amyl-disulphocarbonates have come into use for this purpose.

Potassium amyl-disulphocarbonate is said to have proved cheapest and most easily prepared by simply bringing together, with precautions against too great rise of temperature,

a strong solution of potassium hydrate, amyl alcohol of fusel oil, and carbon disulphide.

*Arsenic acid* — has come to be largely manufactured to be used in the conversion of commercial aniline oil into fuchsine, common arsenious oxide being treated with boiling nitric acid, or dissolved in hot hydrochloric acid and submitted to the action of a stream of gaseous chlorine. The recovery and utilization of the arsenic from the residues of fuchsine production has been attempted in various ways, none of them quite satisfactory on both economic and sanitary grounds. Sodium arseniate constitutes a large portion of the "dung substitute" used by calico-printers in developing sharp, well-defined patterns with clear grounds, and has come to be made on a pretty large scale by treating arsenious oxide with strong soda-lye, evaporating and fusing the residue with sodium nitrate.

*Oxygen gas.*—The nearest approach to a process fit for successful technical use in making gaseous oxygen upon a large scale is undoubtedly that of Tessié du Motay, consisting in exposing sodium manganate at a low red heat to a current of superheated steam, reproducing the manganate from the residue of manganese sesqui-oxide and sodium hydrate by passing purified air over it at the same temperature. The cost of the gas is still far from having been reduced to the point at which it might be, with great advantage, used for many industrial purposes, notably in the manufacture of sulphuric acid in closed chambers; but the gas may be said to have acquired a certain commercial foothold, and its application in some directions has been facilitated by the system of storing it under a pressure of several atmospheres in portable iron cylinders. In giving control of a temperature at which platinum and iridium may be melted into large ingots, in affording the means of producing light of an intensity comparable with that more commonly now derived from an electric current, and under conditions sometimes more conveniently available than the latter, and in its medicinal application the gas has already rendered useful service. Under this last head the notices in some scientific works and reports of late years have tended to give an unduly depreciated idea of the therapeutic value of the substance. While the old notion of the respiration of pure oxygen having any *chemical* value is of course no longer entertained, the relief which may be afforded a patient in the advanced stages of phthisis, in pneumonia and any other affection interfering in a purely mechanical way with the volume of air with which the lungs can be effectively supplied, if once witnessed, will not be underrated or denied.

The preparation and sale, in similar compressed form, of nitrogen monoxide for dentists' use, and of hydrogen for employment with oxygen in the production of the "calcium

light," have become common, though upon no very great scale. For making hydrogen industrially the plan of Tessié du Motay is worth notice — namely, heating surplus carbon with slaked lime, giving rise to the reaction  $\text{Ca}(\text{HO})_2 + \text{H}_2\text{O} + \text{C} = \text{CaCO}_3 + 2\text{H}_2$ , and reproducing calcium hydrate by passing steam over the heated carbonate which has been formed. Save for a few special purposes, as occasionally for filling balloons so as to give them unusual ascensive power, it seems unlikely that the place of pure hydrogen in industrial applications cannot be equally well or better taken by the gaseous mixture which contains it along with carbon monoxide, nitrogen, &c., known as "water gas" or "generator gas."

Many other substances might be named which have gradually been passing, under the eyes of those still of the present generation, from the domain of the scientific or the pharmaceutical laboratory into that of the manufacturing chemist. There seems no reason to doubt that *ozone* has for some time been more or less experimentally used in bleaching sugar, while hydrogen dioxide has been brought into the market as the "Eau de la Fontaine de Jouvence" for partially destroying the color of human hair, pending any serious use of it in bleaching textile fabrics. *Nitrous acid* and *nitrites* have taken rank among the regular working reagents of the maker of coal-tar colors. *Silver nitrate* is made by tons for the purposes of the photographer, as well as for medical and surgical use. The *double salts of ammonium with nickel or cobalt* are consumed in great quantity by the electro-plater, while salts of such rare metals as *vanadium* and *cerium* are regularly applied in the processes of calico-printing.

### Organic Chemicals.

In the production of these much greater changes have occurred, and much greater advances have been made within but few years than has been the case in regard to inorganic materials. Most of the substances in question, however, find their application in connection with particular arts, and are better considered in relation to these. A few may be noted here.

*Methyl alcohol* has long been used as a solvent, but more largely than ever with the progress of manufacturing organic chemistry, and under the influence of revenue laws permitting ordinary alcohol, when mixed with this wood spirit, to be used without heavy taxation. In the coal-tar color industry, moreover, methyl alcohol itself and several of its derivatives play an important part. For the production of the methyl acid derivatives of rosaniline, &c.,

*Methyl chloride* has taken the place of the dangerous methyl

nitrate and to some extent of the more expensive iodide, without, however, displacing altogether the latter, and has also been brought into use as one of the materials for the production of artificial cold by rapid evaporation in closed vessels.

*Ethyl alcohol* up to almost "absolute" strength and well freed from foreign alcoholic and other impurities, can now be had in commerce, distilled in apparatus capable of more rapid and delicate fractional separation of the distillates than was industrially common not long ago. Amongst the more extensively prepared products from ordinary alcohol,

*Ether* and *chloroform* are made chiefly by processes long in use, and which have undergone no important modification of late (chloroform is made to a small extent from chloral hydrate), but greater pains are taken with the final purification, sometimes now carried out by other hands than those which have turned out the crude product, and a much higher and more uniform standard of purity has consequently been attained by the best makers for medical and surgical use.

*Chloral hydrate* has taken its well recognized place among therapeutic agents and become an article of regular manufacture upon a very large scale. In a much smaller way *iodoform* has also entered the field of industrial production.

*Ethyl iodide* and *bromide* enter largely into the resources of the coal-tar color maker, and the latter, as above noticed, has been made the means of safely transporting bromine, to be afterwards recovered in the free state, if desired, with regeneration of ordinary alcohol.

*Amyl alcohol* has ceased to be regarded solely as a mischievous impurity of distilled spirits, and has, with some of the compounds obtainable from it, come to find useful applications. Amylated derivatives of rosaniline and allied color bases are made from the iodide, bromide and chloride, while *amyl nitrite* and *valerianic acid*, with its salts, have become common products for medical use.

Few substances have acquired more widely extended importance than *glycerine*, both on account of its special or individual properties and those which, in modified form, it shares with bodies earlier known and used. Its history, however, rather belongs with that of the fats from which it is derived.

The manufacture of *phenol* or *carbolic acid* has developed a distinct branch of the many-sided industry of coal-tar, and in beautifully pure, colorless, crystalline form replaces the coarse, dark-brown "coal-tar creosote" which alone was known but a few years ago.

*Cresol* and *thymol* have also become regular articles of manufacture.

*Benzoic acid* is said to be still made to some extent from benzoin, or perhaps partly from Australian "acaroid resin"

(of *Xanthorrhoea hastilis*), but is mainly and largely obtained by evaporating the urine of herbivorous domestic animals and boiling with hydrochloric acid to decompose the hippuric acid present. Some is also produced in France, by Poirrier and others, by continuous boiling of benzyl chloride with strong nitric acid. The conversion of naphthaline into phthalic acid, and this into benzoic, seems to have proved on the large scale less advantageous. Beside the consumption of benzoic acid in making the artificial colors for dyers' use, there is reason to believe that it enters to some extent into the composition of the secret nostrums used in flavoring manufactured tobacco.

*Salicylic acid* may more properly be considered in its special relations among antiseptics. Its synthetic production by Kolbe's process from phenol-sodium and carbon dioxide represents one of the most admirable gifts of pure chemistry in modern times to medical, sanitary and industrial progress.

*Phthalic acid* is another of the products called for by the maker of artificial chemical dye-stuffs. The use of its anhydride in the development of eosine and the other beautifully colored derivatives of Baeyer's phthaleins has led to its being itself largely made from the naphthaline which was so long associated almost solely in chemists' minds with the classical "light-bearing" researches of Laurent.

In connection with the same great field of the last twenty years' work upon the colored products obtainable from tar, innumerable chlorinated and brominated derivatives of hydrocarbons, phenols, acids have been made upon a larger or smaller scale; and of late still more extensively organo-sulphonic acids, but for the most part these have not formed the final products of separate chemical manufactures, but have constituted single steps in the work of the producers of the dye-stuffs themselves.

In regard to the treatment of the *natural vegetable alkaloids* recent times have not been without their evidences of progress. Attention has been given to improving, both in quantity and quality, the supply of original material, notably in the direction of cinchona cultivation under Dutch and English auspices in Java and Southern India, and in connection with such efforts chemistry has aided in some measure as a guide to practice. The scale upon which *quinine*, *morphine*, *strychnine* and *atropine* were formerly made has undergone very great extension, and although no radical change has probably been made in the processes by which these alkaloids are extracted, the final purification has been much improved, especially as to the more easily alterable bases, and new solvents have served to cheapen the processes and facilitate crystallization. The other cinchona alkaloids which accompany quinine have, either singly or in admixture, been brought to some extent into use instead of merely accumulating them as worthless

by-products. Some new substances of this class have been made available for medical purposes and are added to the list of those manufactured, as for example, the *eserine* of Calabar bean; while among the products of chemical alteration *apomorphine* has been found valuable. Researches of a purely scientific character upon the less known substances classed as vegetable alkaloids, but turning out to be in some cases complex mixtures, as aconitine and veratrine, promise to yield results before long of practical applicability.

#### MECHANICAL APPLICATIONS OF CHEMICAL MANUFACTURES IN GENERAL.

Among the chief directions of improvement in the "plant," appliances, and physical methods of working of chemical factories may be noted:

*Improved grinding mills*, especially those run at comparatively high speed and aiming at true grinding rather than crushing.

The extended use of *steam coils* and *steam jackets* for heating purposes, admitting of complete control and nice regulation of temperature.

*Heating by vapor from materials under treatment*, such an adjustment being made of the different portions of the work as to permit of this utilization of otherwise waste heat, and sometimes allowing of simplification in the working itself.

*Heating under pressure* greater than that of the atmosphere, the use of so-called "autoclaves," often arranged with special ingenuity as to the details of filling, emptying, observing the progress of reactions occurring within, &c., playing an important part in some of the branches of modern chemical industry.

The use of "ice machines" for the *production of artificial cold*. These valuable machines have lent most important aid in various directions, enabling results of solidification, crystallization, rapid cooling to determinate temperatures, &c., to be secured in climates and seasons, and under temporary conditions of weather which would otherwise prove serious if not insuperable obstacles. In many cases uniformity of working is gained by the control thus given of temperature in the downward, as formerly in the upward, direction. In turn, manufacturing chemistry has been called upon to supply the materials used in most of these machines to produce cold by evaporation, as ethyl and methyl ethers, methyl chloride, petroleum spirit (mainly butane), ammonia and sulphur dioxide, the machine working with air alternately compressed and expanded alone using a material furnished by nature.

*Improved mechanical arrangements for agitation or stirring of liquids*, including under this head not only revolving paddle-

arms and the like contrivances, but the blowing in of air or steam, often now made to accomplish the work of stirring and mixing, and at the same time that of heating, oxidation, &c.

Extended use of *vacuum pans* for evaporation, with or without arrangements for condensing the vapor given off. The vacuum pan has long ceased to be a part only of the special plant of the sugar refinery, and has become one of the well recognized appliances of the general manufacturing chemist, without which much of the treatment of the more delicate and easily alterable materials he has to deal with could with difficulty be accomplished.

*Improved apparatus for distillation*, especially that intended to effect nice fractional separation of liquids differing often but little in boiling point. The extension upon a manufacturing scale of the processes of organic chemistry has given to this increased importance.

Introduction of the method of *distillation by means of, or along with super-heated steam*. In certain cases this enables a simple physical purification of special materials to be effected which otherwise would require elaborate and tedious chemical processes to be used.

The general application of "*centrifugal machines*" or "*hydro-extractors*" for draining and washing suitably divided solid materials, especially crystals. The quickness and thoroughness with which the work is done, and the limited amount of wash-water or other fluid necessary, constitute important advantages.

The use of *filters arranged to work with a partial vacuum*, so as to expedite filtration and leave the solid residue in a more effectually drained condition.

The use of *filter presses* to mechanically squeeze out the liquid tenaciously retained by precipitates, sediments, skimmings, &c. These have been much improved of late by the general substitution of metal for wood in their construction, the increased pressure obtainable—commonly up to 120 or 130 lbs. per square inch—the rapidity with which the pressure is brought to bear and the readiness with which it may be regulated, the thoroughness with which a small quantity of washing fluid may be made to remove residual soluble matter, and the substantial and durable character given to the framework and mechanism. In a multitude of cases chemical industry has derived most valuable aid from these useful pieces of mechanism in their more modern forms.

J. W. MALLET.

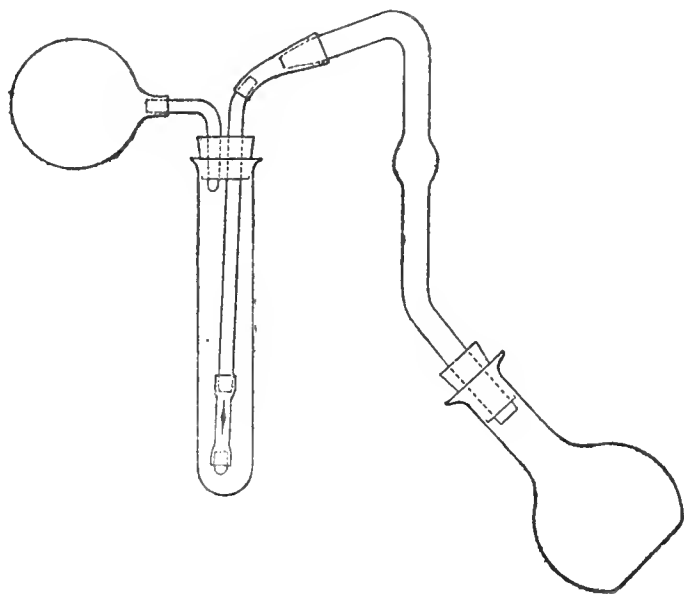
(To be continued.)

*NOTES.*

*A New Form of Absorption-Apparatus for Use in Estimating Ammonia.*

In attempting to estimate ammonia by the process which involves its expulsion from its compounds by the action of boiling solutions of caustic alkali and its collection in hydrochloric acid, it frequently happens, even when great precaution is taken to prevent it, that, on account of the difficulty of regulating the evolution of the gas, small amounts of ammoniac chloride are carried with escaping air through the absorption bulbs in ordinary use, and discharged visibly from the apparatus, such loss introducing more or less inaccuracy into the determination of ammonia when it is made to depend upon the amount of ammoniac chloride retained within the apparatus, whether this is weighed directly or estimated indirectly after precipitation as ammonio-platinic chloride.

The difficulty may be overcome by the use of a very simple apparatus of the following construction: Through a perforated rubber stopper fitted to the mouth of a flask having a capacity of 70 cm.<sup>3</sup> or 80 cm.<sup>3</sup> passes a glass tube of about 0.7 cm. interior diameter, about 20 cm. long, and bent as shown in the accompanying figure. About midway of the vertical



part, which has a length of 10 cm., the tube expands to a small bulb, and at the upper end it is joined by means of a rubber connector to a second tube, which passes through a doubly-perforated stopper fitted to the mouth of a test-tube holding about 30 cm.<sup>3</sup>, and ends in a valve consisting of a piece of rubber tubing closed at the lower end with a bit of glass rod and pierced with a longitudinal slit. Through the second perforation of the stopper of the test-tube passes a tube, as shown in the figure, over whose outer end the neck of a small rubber balloon (such as are sold in the shops attached to toy-whistles) is drawn and securely fastened. The apparatus when thus put together must be air-tight.

When a determination of ammonia is to be made with the aid of this apparatus, the test-tube is filled to a point somewhat above the valve with dilute hydrochloric acid and placed in a vessel of cold water; the ammonia salt is put into the flask with a bit of platinum foil (to secure quiet ebullition), and 20 cm.<sup>3</sup> or 30 cm.<sup>3</sup> of a sufficiently strong solution of sodic or potassic hydrate; heat is applied to the flask and its contents rapidly boiled until the greater part of the water has been converted into steam and the ammonia completely driven over with the steam through the valve (which prevents the return of any part of the liquid in the test-tube when the pressure wavers) into the hydrochloric acid — the air which filled the apparatus in the beginning now collecting, together with that portion of the ammoniac chloride which escapes detention in the acid, in the upper part of the test-tube and in the balloon, which it distends.

The action proceeds quietly and no special care is required during the operation. The flask being properly inclined, and the conducting tube of suitable size, there is no danger of a transfer of solid matter from the flask to the absorption-tube by the agency of bubbles ascending the conducting tube; for, under these conditions, bubbles rarely appear at all in the conducting tube and could never by any possibility pass the bulb.

At the end of the operation the tubes are disconnected at the rubber joint, the stopper of the test-tube loosened to permit the balloon to collapse, and the contents of the test-tube, together with the rinsings of the test-tube and its accessories — the washing of the interior wall of the balloon, upon which some small amount of ammoniac chloride has fixed itself, being easily accomplished by throwing a fine stream of water into the balloon through its connecting tube and ejecting it again by pressure upon the exterior — transferred to an appropriate receptacle and treated in one or another of the usual ways.

The chief points of the device are its effectiveness, convenience and simplicity; and these qualities may render its application in other analytical processes equally advantageous.

F. A. GOOCH.

*Glucose.*

It is known that saccharose combines with bases giving sucrates, while glucose by treatment with alkalis yields glucic acid, which differs in composition from glucose by the elements of water, and melassic acid, which is allied to the ulmic compounds. PÉLIGOT has found the following new facts: Glucose obtained from starch or by the action of acids upon sugar combines with lime, forming unstable products which are rapidly transformed into others. Lime dissolves largely in water containing 15–20 per cent. of glucose. The solution is at first alkaline, but gradually loses its alkalinity, becomes brown and finally deposits a yellow substance, sometimes of crystalline appearance. The same precipitate, more strongly colored, is produced quickly by boiling the filtered solution. Under these circumstances there is formed glucate of lime, part of which remains in solution and can be separated by sub-acetate of lead. At the same time another substance is formed which has escaped the notice of the author and other chemists who have worked with these substances for more than forty years. Accident revealed it to the author. Resuming the somewhat neglected study of glucic acid, he found in a kind of molasses, obtained as a by-product in the preparation of the acid, fine prisms which he first mistook for glucic acid. This led to further attempts, which were successful, to get the substance in this form. These crystals have the composition of saccharose,  $C_{12}H_{22}O_{11}$ , but the substance is not sugar; it does not ferment with yeast, and is not sweet, but rather bitter to the taste. The author calls it *saccharine*. It is distinct from the other substances having the composition of sugar, is not easily soluble in cold water, and is in large part volatile. Nitric acid, 36° Beaumé, and concentrated sulphuric acid hardly act upon it, nor does it reduce ammonio-cupric tartrate except by long boiling. It crystallizes very readily when pure. The author is inclined to think that the sugars instead of being polyatomic alcohols are esters, and that this action with lime is a true saponification. He surmises that saccharine may prove to be an alcoholic substance.—(*Compt. rend.*, Dec. 1st, 1879.)

*New Metals.*

In the *Comptes rendus* for Oct. 22, 1878, Marignac announced the probable existence, in the *erbia* of Bunsen and Clève extracted from gadolinite, of a new earth, the oxide of a metal for which he suggested the name *ytterbium*. The small amount of material which he possessed prevented the complete study of the substance, but he was able to describe certain properties which he considered established its individu-

ality. He gave provisionally the molecular weight 131. Its spectrum was studied by Soret. Nilson of Upsala then took up the subject, having larger quantities of material at his command, and was able to isolate and study chemically pure *ytterbia*. He found the molecular weight of the oxide 131.92 and 132.17. Thalén studied the substance spectroscopically in connection with Nilson, and his work tended to show the presence of still another new earth. The latter Nilson called *scandia*, and made a partial chemical examination of it, finding its molecular weight below 90, calculated for  $\text{ScO}$ .<sup>\*</sup> Subsequently Clève extracted scandia from gadolinite and yttrite of Norway, and studied it more fully. He found that the only oxide of scandium was  $\text{Sc}_2\text{O}_3$ , and the atomic weight of the metal 45. This was so much smaller than Nilson's number that he suspected the presence of another earth. But Thalén examined its spectrum and pronounced it pure scandia. Nilson's substance must hence have been mixed with seven or eight times its weight of ytterbia. Clève gives an extended chemical description, and shows that it corresponds almost completely, point for point, with the description given by Mendelejeff of the hypothetical metal *ekabor*, of atomic weight 44.

Soret, when studying the spectrum of ytterbia, as mentioned above, was led to suspect the presence in erbia of another new earth besides ytterbia, and designated it provisionally as X. The probable existence of such a substance had been indicated by Delafontaine and Marignac. Subsequently Delafontaine gave the name *philippia* to a substance found by him and considered identical with Soret's X. He gave a partial chemical and spectral description in *Comptes rendus*, Oct. 14th, 1878, stating provisionally the molecular weight of the oxide as 90-95. Soret admits himself unable† upon the publications of Delafontaine to affirm or deny the identity of philippia with X, but is inclined to consider them identical. He thinks the existence of X well established.

Clève has given reasons based principally upon study of spectra for supposing that erbia contains, besides ytterbia and scandia, three different earths, which he named *erbia*, *holmia* and *thulia*.‡ But Lecoq de Boisbaudran and Soret both pronounce the spectrum of holmia identical with that of X.§ Soret had also called attention, in connection with X, to the lines which Clève describes as characteristic of thulia, but he did not consider the indications of the spectra alone as sufficient evidence for the announcement of a new element. Lecoq de Boisbaudran says his own studies, not yet completed, tend to confirm the idea of Soret, Clève and Thalén.

Delafontaine has claimed the discovery of still another

\* *Compt. rend.* March 24th, 1879.

† *Ibid.* Sept. 1st, 1879.

‡ *Ibid.* Sept. 15th, 1879.

§ *Ibid.* Sept. 15th, 1879.

earth in samarskite, which he calls *decipia*. He has given a description of its spectrum,\* and indicated its approximate molecular weight as 122.

The same investigator, followed by Lecoq de Boisbaudran and Soret, has found in the spectrum of the earth known as didymia evidence tending to show that the substance contains at least two different earths. And Lecoq de Boisbaudran obtaining still more definite results, has proposed the name *samaria* for one of them.

Lawrence Smith announced to the French Academy, September 22d, 1877, the discovery of a new earth in samarskite, which he called *mosandra*. But Marignac and Delafontaine, who examined the substance, pronounced it identical with the *terbia* of Mosander.† September 1st, 1879, Smith states that he has not yet obtained the earth in a satisfactory state of purity, but claims that it differs from *terbia*. As it does not give absorption bands, he is obliged to depend upon chemical study.

July 7th, 1879, Hiortdahl announced to the same body the discovery of a new earth designated as *norvegia*, but gave no description.

#### *On Coto Bark and its Constituents.*

JOBST and HESSE have recently subjected the genuine coto bark from Bolivia to a careful examination, and have established a number of valuable facts concerning it. Without entering into a detailed description of their results, we may call attention to a statement made in the original paper which may prove of very great interest to the general public. The bark has the reputation in Bolivia of being an excellent remedy in cases of intestinal diseases. DR. V. GIETL concludes, as the result of an extensive experience in the use of this material, that it is a *specific against diarrhœa in its different modifications*. DR. BURKART has shown that the bark and the tincture cause certain objectionable after-effects if taken into the system. On the other hand, *paracotoïn*, which can be prepared from the bark, and which is described by Jobst and Hesse, is an excellent remedy. A number of cases are cited illustrating the beneficial effects of administering it in cases of chronic diarrhœa and Asiatic cholera.—(*Ann. der Chemie*, 199, 82.)

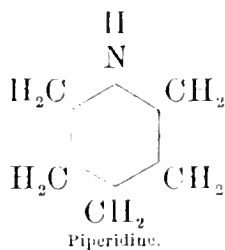
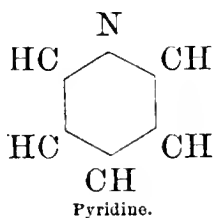
#### *Transformation of Piperidine into Pyridine.*

In the last number of this JOURNAL attention was called to the fact that pyridine and its homologues have of late been the subject of a number of investigations most of which tend

\* Compt. rend. Oct. 28th, 1878.

† Ibid. Aug. 12th, Oct. 22d, 1878.

to show that there exists close relation between the natural alkaloids and the pyridine series. A short time ago Hofmann showed that a product can be obtained from piperidine which resembles very closely one obtained from pyridine. Though this fact indicated a close relation between pyridine and piperidine, no transformation has hitherto been effected which proves the relation. KOENIGS has now succeeded by a simple process in transforming piperidine directly into pyridine. It is only necessary to heat the former with sulphuric acid at  $300^{\circ}$  for about seven hours. The change effected is one of oxidation. It is suggested that the piperidine,  $C_5H_{11}N$ , bears to pyridine,  $C_5H_5N$ , the relation of an addition-product. Assuming Koerner's formula for pyridine to be correct, the relation may be expressed thus—



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